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XII. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

§ 1. THE interesting paper read to the Physical Society of London by Dr. J. Rae, the arctic explorer, on the comparative saltiness of freshly formed and older ice-floes*, induced me to examine some of the physical properties of brine and some other of the aqueous solutions of the salts of the sea. This examination has extended itself to some other salts; for before attacking the problem of the freezing of sea-water, the composition of which may be little less complex than that of the earth itself, it seemed advisable to enrich our knowledge of the properties of the solutions of some of its more abundant constituents in the separate form. Some of the experimental results unexpectedly opened so wide and fascinating a field of inquiry, that I have been compelled to make some sort of survey of it; and though the results there gathered are of sufficient interest to be considered by themselves as physical facts, they will assuredly also be concerned in the establishment of a sufficient theory of thalattology.

* Proc. Phys. Soc. May 9, 1874. Phil. Mag. July 1874, p. 56.

Chloride of Sodium.

§ 2. Being fortunately in possession of a large quantity of extremely pure rock-salt in fine crystals, I satisfied myself by the spectroscope of the absence of potassium and lithium. By the usual tests, magnesium and sulphuric acid were also shown to be absent. A determination of the chlorine agreed so closely with the theoretical quantity that not more than 0·2 per cent. of any metal having an atomic weight differing by more than 5 from that of sodium could be present, supposing it to be a chloride. On converting the chloride into a sulphate an equally accordant result was got. This convinced me that I had a perfectly pure substance.

§ 3. *Preparation of the Brine.*—The clearest lumps of the rock-salt were washed in common and then in distilled water. With these a large beaker was filled. Distilled water was poured on so as to fill the beaker about two thirds. If part of the salt is thus always above the surface of the brine, the latter appears to be saturated in twenty-four hours. After forty-eight hours the brine was poured into another beaker and allowed to stand until crystals began to be formed. It was then transferred to a stoppered bottle and was ready for use. Although Regnault and others have shown that for temperatures above 0° C. the solubility of chloride of sodium in water is constant, yet the precaution was taken of suspending a muslin bag containing some crystals of salt from a string passing through the cork of the bottle so that the crystals touched the surface of the brine. By this means the perfect saturation of the brine was assured. At 18° C. this solution contained 26·2724 per cent. of salt. The solution was weighed in a long-necked flask, and was evaporated to dryness and heated to about 300° C.

The following numbers show the results obtained by some other experimenters :—

			per cent.	spec. grav.
Kopp	. .	Sat. at 25° C. contains	26·32	
Kastner	. .	„ 18·75	„ 26·72	1·2046
F. G.	. .	„ 18	„ 26·27	
F. G.	. .	„ 21		1·1997
F. G.	. .	„ 26		1·2011

The above specific gravities are referred to water at the same

temperature as the brine, as far as my own experiments are concerned.

§ 4. *Cold produced on mixing saturated Brine with Water.*—To examine this point, a series of covered beaker-glasses containing known weights of water, and a similar series containing saturated brine, were placed side by side in a tin tray containing water and resting on flannel. The whole arrangement was covered with flannel and allowed to stand over night. In the morning the temperature of eight or ten was found to be exactly 21° C. The liquids were prepared by measuring out from a burette in proportions that, taking 1.1997 as the specific gravity of the brine, the ratios by weight were as in columns 3 and 4 (Table I.). The experiments were performed by taking out a water-beaker, rapidly drying its outside, pouring in the brine, stirring with the thermometer, and at once reading.

TABLE I.

Cold produced on mixing saturated Brine with various proportions of Water by weight. Initial temperature 21° C.

(1) Water, in grams.	(2) Sat. brine, in grams.	(3) Water, per cent.	(4) NaCl, per cent.	(5) Fall of tempe- rature.
				$^{\circ}$ Cent.
60	140	81.611	18.389	0.4
65	135	82.268	17.732	0.5
70	130	82.925	17.075	0.6
75	125	84.081	15.919	0.75
80	120	84.238	15.762	0.8
85	115	84.895	15.105	0.85
90	110	85.552	14.448	0.9
95	105	86.198	13.802	0.85
100	100	86.870	13.130	0.85
105	95	87.522	12.478	0.85
110	90	88.289	11.821	0.85
115	85	88.835	11.165	0.9
120	80	89.492	10.508	0.9
125	75	90.149	9.851	0.9
130	70	90.806	9.194	0.9
135	65	91.463	8.537	0.75
140	60	92.119	7.881	0.65
145	55	92.776	7.224	0.6
150	50	93.433	6.567	0.6
155	45	94.089	5.911	0.6
160	40	94.746	5.254	0.5

The greatest depression of temperature accordingly in the

range of ratio between 84 and 90 of water and 16 and 10 of salt, and the greatest depression of temperature to be got by mixing saturated brine with water, is under no circumstance quite 1° C.

§ 5. If now anhydrous salt on dissolving in water absorbs heat only by reason of its conversion into a liquid, and if no hydrate of salt exists at the ordinary temperature above 0° C., no such absorption of heat as we have seen to occur could ensue on mixing brine and water. Two series of experiments are therefore at once demanded:—the first to see what proportion must exist between anhydrous salt and water to absorb the most heat; the second to see if at any ratio between salt and water an abnormal change of density takes place.

§ 6. *Cold produced on mixing NaCl with Water.*—A quantity of rock-salt having been finely powdered, was passed through muslin so as to be quite mealy. Various quantities of distilled water were weighed into beakers, and various quantities of the rock-salt were thrown in under constant stirring. The abasement of temperature being noted gave the results of Table II. The temperature of the salt was about 2° C. above that of the water. And it is seen that the greatest abasement of temperature occurs when there is about 40–60 of salt to 160–140 of water (say 25 per cent. of salt). This result is what we should expect, remembering that the saturated solution contains 26·27 per cent. of salt.

TABLE II.—Maximum Cold produced on mixing Salt and Water in different proportions by weight.

Temp. of salt = $20^{\circ}\cdot 2$ C.

Water, in grams.	NaCl, in grams.	Temp. of water.	Temp. of mixture.	Fall.
190	10	19·1	18·0	1·0
180	20	18·4	17·0	1·4
160	40	18·4	16·4	2·0
140	60	18·4	16·3	2·1
120	80	18·4	16·5	1·9
100	100	18·5	16·7	1·8

§ 7. *Specific Gravity of Brines of various strengths.*—The question as to the source of cold when brines are diluted can be conveniently approached from an examination of the density of

brines of different strengths, and the comparison between the observed specific gravities and the theoretical specific gravities, supposing no change of volume to take place. The brine was found to have a specific gravity of 1·2011 at 26° C., the temperature at which the determinations were made. In Table III. the columns 1 and 2 give the weights in grams of the quantities of water and saturated brine. Columns 3 and 4 give the percentage of the water and NaCl in the resulting brines. Column 5 gives the specific gravity found, and column 6 gives the specific gravity calculated under the hypothesis that no alteration of volume ensues.

TABLE III.—Specific Gravity of Brines of various strengths.

(1) Water, in grams.	(2) Saturated brine, in grams.	(3) Water, per cent.	(4) NaCl, per cent.	(5) Observed spec. grav.	(6) Calculated spec. grav.
0	∞	73·73	26·27	1·2011	
60	140	81·61	18·39	1·1087	1·1328
70	130	82·92	17·07	1·0963	1·1211
80	120	84·24	15·76	1·0874	1·1117
90	110	85·55	14·45	1·0800	1·1014
100	100	86·87	13·13	1·0725	1·0914
110	90	88·29	11·82	1·0650	1·0815
120	80	89·49	10·51	1·0574	1·0718
130	70	90·81	9·19	1·0501	1·0621
140	60	92·12	7·88	1·0428	1·0530
150	50	93·43	6·57	1·0357	1·0434
160	40	94·75	5·25	1·0284	1·0347
170	30	97·06	3·94	1·0246	1·0258

There is accordingly an increase of volume when a solution of salt is diluted; and this is of course connected with the absorption of heat examined in § 4, Table I. When the original temperatures are restored, a mixture of strong brine and water may have a volume two hundredths greater than the sum of the volumes of its constituents. And when the brine contains as little as 4 per cent. of salt, its specific gravity is sensibly smaller than if such a proportion had been the result of the mixture without contraction of the strongest brine and water.

§ 8. *Refraction of Light by Brines of different strengths.*—It seemed, from a consideration of the numbers in Table III., that at or near the point of saturation a definite hydrate of salt exists;

and that this is not merely diluted, but also actually decomposed on the addition of water, so that expansion takes place. This I imagined might be tested by the change in the refractive index of the brine. Accordingly brines of various strengths were placed in a hollow prism of 60° . The refraction was measured on a goniometer (Babinet's) table provided with telescope and collimator. An alcohol-flame containing sodium was employed as a source of light shining through a very fine slit. The minimum refraction being obtained, the D line was split by the spider-thread. In Table IV. the empty prism is considered as giving a displacement of 0° . The angular displacements are alone here given, as they perfectly suffice for the detection of singular values.

TABLE IV.

Refraction of Light by Brines of various strengths.

Temp. = 22° C.

Per cent. of brine in solution.	Per cent. of salt in solution.	Displacement.	
∞	26.27	$27^\circ 0' 45''$	or 27.0125
70	18.39	26 2 30	„ 26.0416
65	17.07	25 44 0	„ 25.7333
60	15.76	25 32 30	„ 25.5416
55	14.45	25 20 0	„ 25.3333
50	13.13	25 10 0	„ 25.1666
45	11.82	24 59 0	„ 24.9833
40	10.51	24 48 0	„ 24.8000
35	9.19	24 37 30	„ 24.6250
30	7.88	24 26 45	„ 24.4458
25	6.57	24 16 30	„ 24.2750
20	5.25	24 6 0	„ 24.1000
0	0.00	23 23 0	„ 23.8833

These numbers show a singular value at about the 10- to 11-per-cent. solutions.

§ 9. Another method of attacking the question is offered by the examination of the boiling-points of various brines. Accordingly I took solutions made by mixing saturated brine with water, and waiting for a day on which the barometer stood nearly at the mean, I determined the boiling-points of the brines. The vessels were tall copper cylinders. In the Table V. the temperature of the steam as well as that of the brine itself is given. The boiling was, of course, only continued a short time to avoid the error of strengthening the brine.

TABLE V.

Boiling-points of Brines of various strengths in copper cylinder.

Per cent. of NaCl.	Boiling-point in liquid.	Boiling-point in vapour.
26·27 (sat.)	108·8	107·0
18·389	104·7	104·2
17·075	104·2	103·1
15·762	104·0	102·6
14·448	103·4	102·5
13·130	103·0	102·3
11·821	102·6	101·9
10·508	102·4	102·1
9·194	102·0	101·7
7·881	101·7	101·3
6·567	101·2	101·0
5·254	101·0	101·0
0·00 (dist. water)	100·4	100·0

We have here again a singular value about the 10- to 11-per-cent. solutions.

§ 10. *Freezing-points of Brines of various strengths.*—The molecular separation of water from salt when a brine is boiling has to some extent a counterpart in the separation of ice from brine when the latter is subjected to cold. If a weak brine such as 9 of water to 1 of saturated brine (that is, 1 of salt to 24·2 of water) is subjected to cold, pure ice begins to be formed in this case at $-1^{\circ}5$. The temperature gradually sinks; but, as has been shown, the solid part consists of ice, which may be completely freed from salt by mere pressure. This formation of ice continues, and the temperature sinks until the inferior limit attainable by an ice-salt freezing-mixture is reached (-22° C.). The brine, of course, becomes richer and richer in salt. In other words, brines richer in salt yield up ice at lower temperatures. Thus, in Table VI. The same brines are examined as were examined in the preceding Tables. The various brines were examined in succession, being contained in small beaker-glasses in an ice-salt freezing-mixture. It is noteworthy that all the brines are supersaturable in regard to ice, so that the temperatures are most exactly determined by two observations. A good deal of ice is allowed to form, and this is then suffered nearly entirely to disappear; the temperature is observed at

which the ice begins to increase in quantity when the brine is again subjected to cold.

TABLE VI.

Temperatures at which Brines of various strengths give up ice.

(1) Water, in grams.	(2) Brine, in grams.	(3) Per cent. of NaCl.	(4) Temperature at which ice is first formed.
60	140	18.389	-15.4
70	130	17.075	-15.0
80	120	15.762	-12.4
90	110	14.448	-11.1
100	100	13.130	-9.4
110	90	11.821	-7.7
120	80	10.508	-7.7
130	70	9.194	-6.7
140	60	7.881	-5.4
150	50	6.567	-4.1
160	40	5.254	-3.4
180	20	2.627	-2.1
185	15	1.970	-1.5
190	10	1.313	-1.9 (?)
195	5	0.656	-1.5
200	0	0.000	0.0

Again the brines which contain 10 to 11 per cent. of salt have singular behaviour in regard to the temperature at which they yield ice. These are the very solutions, it will be remembered, which behave singularly in respect of their refractive indices and also of their boiling-points. On comparing with Table III., this singularity does not manifest itself in regard to the specific gravities.

§ 11. *Effect of cooling saturated Brine.*—It is seen from Table VI. that, as far as the strengths of brine there examined extend, the stronger the brine the greater the cold required to separate ice from it. The strongest brine there examined contains 18.389 per cent. of NaCl. If saturated brine (containing 26.27 per cent. of NaCl) be cooled, quite a different class of phenomena ensues. Down to 0° C. no solidification whatever ensues either of ice or of salt. At -7° crystals of the bihydrate are observed to fall ($\text{NaCl} + 2\text{H}_2\text{O}$). These present a beautiful appearance of iridescent scales heavier than the mother-brine.

Their composition has been examined by Löwitz, Fuchs, Nölle, and Mitscherlich, whose analyses, however, are not in good accord, that of Löwitz being as much as 10 per cent. different from the calculated percentage of the bihydrate. Ehrenberg and Frankenheim state that the same hydrate is produced when a dilute solution of chloride of sodium evaporates at 15°C ., and that it suddenly converts itself into the cubical anhydrous salt and water. At -22°C . the whole of this hydrate appears to be removed. The gradual impoverishment of the mother-brine was tested by maintaining a brine, at first saturated, for half an hour at the successive temperatures -10° , -16° , and -21 to -22°C . The brine had been previously kept at 0° for an hour. The original brine contained 26.2724 of NaCl per cent. It was the mother-brine from each crop of crystals which was subjected to the lower temperature.

		per cent.
Saturated brine at 0°	contained	26.2724 of NaCl.
Mother-liquor after keeping at -10°	„	24.6528 „
„ „ -10°	„	24.6187 „
„ „ -16°	„	24.1182 „
„ „ -21° to 22°	„	23.8874 „

It is clear, therefore, that down to -21° the solidification impoverishes the brine,—a result which might be due to the formation of the bihydrate or the precipitation of the anhydrous salt, but which is inconsistent with the formation of ice alone. The determinations were made by weighing 10 or 12 grammes of the brines, when at the atmospheric temperature, into long-necked flasks, evaporating and heating to about 300°C .

§ 12. A quantity of brine which had been thus impoverished by being kept for an hour at -21° to -22° was decanted into another flask and further cooled by contact with solid carbonic acid and ether. The whole (3 or 4 ounces) solidified; and the temperature remained perfectly constant at -22° to -23° (say -23°) until the last drop had frozen at -23° ; it then sank rapidly.

If the vessel be continually shaken during crystallization, the form of the crystals may be very clearly seen. While the anhydrous salt crystallizes in the well-known cubes, the bihydrate separates as iridescent scales, and the body we are now considering solidifies in acicular bundles radiating from nuclei, and

much resembling in appearance the supersaturated solution of sulphate of sodium when solidifying. It is, however, of a more than pearly whiteness, and finally of complete opacity.

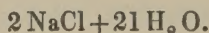
§ 13. To see whether we have here indeed a definite hydrate, the whole was remelted by the warmth of the hand and successively partially refrozen under continual agitation. Each mother-liquor was poured off into a weighed flask and partially solidified, and so on five times in succession. The solid residues were then allowed to melt and get to the temperature of the air; they were then evaporated in the usual way. The portion which remained to the last was not frozen, in order to see whether its composition was the same as that of the parts previously removed by solidification.

TABLE VII.

Percentage of salt in fractionally solidified NaCl brine below 21° .

Temperature of solidification.		per cent.	
-21° to -22°, contained		23·7232 of NaCl.	
-22	„	23·6581	„
-22	„	23·7262	„
-23	„	23·8201	„
-23	„	23·3431	„
-23	„	23·3478	„

The nearest molecular relationship indicated by these numbers is



The formula $\text{NaCl} + 9 \text{H}_2\text{O}$ requires 26·5 per cent. of salt.

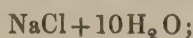
„	$\text{NaCl} + 10 \text{H}_2\text{O}$	„	24·5	„	„
„	$\text{NaCl} + 11 \text{H}_2\text{O}$	„	22·4	„	„
„	$2 \text{NaCl} + 21 \text{H}_2\text{O}$	„	23·6	„	„

§ 14. In these the salient point is the composition of the final mother-liquor, which is essentially the same as that of the successively separated solids.

Accordingly a salt-ice freezing-mixture is just capable of impoverishing saturated brine by withdrawal of salt-rich ingredients (namely the bihydrate) to such an extent that the unsolidified part is homogeneous, in the sense of being solidifiable as a whole. And such solidification takes place immediately below the temperature -21° to -22° , which is the lowest

temperature to be got by an ice-salt freezing-mixture. I presume that if the two solids, ice and salt, could be presented to one another in a state of indefinitely fine division, this proportion of 23·6 of salt to 76·4 of ice would act most promptly and continuously as a freezing-mixture, because the formation of the bihydrate would not then occur.

I am disposed to think that the hydrate of salt, the genesis of which is here described, may have the composition



for under the circumstances of its formation and analysis I only see one serious source of error; and that is the condensation of moisture from the air upon the surface of the cold brine. This would tend to make the amount of salt found too small. To this point we shall have to return.

§ 15. *Physical Condition of a Freezing-mixture.*—The fact that the *rationale* of a freezing-mixture is the liquefaction of solids seems to demand at once the conclusion that a freezing-mixture (of say ice and salt) must always be partially liquid.

Nevertheless, if a mixture be made of about three parts by weight of finely powdered rock-salt and one part of finely crushed ice, the liquefaction which ensues is followed by an apparent regelation so complete that the whole can be handled as a solid mass, and becomes indeed perfectly dry. The cause of this is, I have no doubt, due to the temporary existence of a supersaturated solution of $\text{NaCl} + 2\text{H}_2\text{O}$, a body which is formed at about -10° , Löwitz (-5° , Nölle) (from -3° to -20° continuously, F. G.), when saturated brine is artificially cooled. It is, of course, impracticable to separate this substance from the general mass of the freezing-mixture with sufficient precision to allow of its analysis. The phenomenon of solidification, moreover, only lasts a few minutes. Liquefaction ensues, and the temperature, which had made a pause, again sinks rapidly.

§ 16. The minimum temperature of a salt-ice freezing-mixture seems to be attained between the somewhat wide margins of 3 of salt to 1 of ice, and 1 of salt to 2 of ice. The lowest temperature appears to be -21° to -22° C.

§ 17. *Liquid portion of Freezing-mixture.*—It is clear that the liquid portion of a freezing-mixture is a brine of such a composition as to resist solidification at the temperature of the free-

zing-mixture. Accordingly we ought to find that the liquid portion of a freezing-mixture has the same percentage composition as the mother-liquor of a saturated brine from which the bihydrate has been separated out by the external application of an ice-salt freezing-mixture. To test how far this is verified by experience, dry ice and salt were mingled in three proportions, namely 3 of ice to 1 of salt, 1 of ice to 1 of salt, and 1 of ice to 3 of salt by weight. The salt and ice were in the finest state of division, and the ice was uniformly and as thoroughly dry as possible. The mixtures were constantly stirred in a wooden bowl for ten minutes, and then thrown upon flannel and pressed through.

Ice.	Salt.	NaCl.
3	1	gave a liquid containing 22·508
1	1	24·343
1	3	24·711

The amount of salt found is therefore not far off that contained in the 10 hydrate, namely 24·5.

Cryohydrates.

§ 18. *General.*—The discovery of the hydrate of chloride of sodium which contains about ten molecules of water to one of the anhydrous salt, caused me to look for similar combinations of water with other salts. This was of course all the more necessary, since if such combinations existed with the salts occurring in the sea, and if such combinations had solidifying-points within the range of the atmospheric temperature, the composition of the solid formed when sea-water freezes would be partly that of ice and partly that of the solid hydrates formed from the brine which had been enriched by the removal of water as ice.

§ 19. It has long been known that the presence of a soluble salt in water depresses the point at which the liquid solidifies (irrespective of the nature of the body separated by solidification). Suppose now we take a solution of the salt *a b* saturated at the ordinary temperature and cool it. We may, above 0° C., either get a separation of the anhydrous *a b*, or some crystalline combination of the salt with water, a hydrate. To this Na Cl is the only exception; for this body is equally soluble in water at all temperatures above 0° C. Putting Na Cl on one side, we

may admit, then, that the mother-liquor gets poorer and poorer as the temperature falls. This is obviously the case if the anhydrous salt falls down; and experience informs us that in order to dissolve a hydrated salt, water, and not the anhydrous salt, must be added. Experience also teaches that there is no marked discontinuity at 0°C . We never find the whole of the salt separated before or even at 0°C . One patent consequence of this is that we can form a freezing-mixture (whereof a portion is liquid) by mixing any soluble salt with ice. We get, therefore, in all cases a solution of the salt below 0°C . If as the temperature is still lowered anhydrous salt were to separate out, we should at last get pure water unfrozen below 0°C .—an impossible result. The same would ensue if a hydrate richer in salt than is the solution were to separate out; whereas if ice or a hydrate poorer in salt than is the solution were to separate out, we should then get at a lower and lower temperature a richer and richer solution, and return to the very condition of strength which the lowering of temperature had altered. This is also an impossibility. Accordingly, in all cases some temperature below 0°C . must be reached at which, after separation of the anhydrous salt or a hydrate richer in salt than the solution, the water and salt solidify together, that is, in constant proportion. The effect of such solidification must be (1) the preservation of a constant temperature during solidification from the moment when the proper proportion between the water and the salt is reached; and (2) the preservation of that proportion exhibited by the identity of composition of any crop of the solid and the mother-liquor. It is clear that if ice and the hydrated or anhydrous salt separated out in constant proportion and not combined, but merely mixed with one another, the mass would have a constant solidifying- and melting-point; and this would be below zero to the same amount as would be reached on mixing artificially the anhydrous or hydrated salt with ice in the same proportion. But when we have distinct and unchangeable relation by weight demanded by the constancy of the solidifying- and melting-point, we have undoubtedly a numerical physical relation as fixed, and no less important than the points of fusion or degrees of solubilities. And if, as I shall show, all the hydrates formed under these conditions have distinct crystalline forms, we have all the conditions of chemical associa-

tion; at least I know of none other. It is an essential element in the existence of these compounds that they can only exist in the solid state below 0°C . Hence I propose to call them for the present "cryohydrates." At the ordinary temperatures they melt in their own water of crystallization, and appear as ordinary solutions never saturated. And when once the proportion between the salt and the water in a cryohydrate has been found, the cryohydrate can be formed in any quantity by dissolving the salt in water in the required proportion. Such a solution shows no sign of yielding up ice or anhydrous salt (or other hydrate) until its temperature, on being lowered, reaches a certain temperature peculiar to the salt (unless under supersaturation); it then solidifies as a whole, maintaining throughout that constant temperature. Above this temperature (that is, in the melted state) it is precisely in the same predicament as a salt melted in its own water of crystallization.

§ 20. The same cryohydrates are (and indeed must inevitably be) formed if we cool such a solution of the respective salt in water as contains a greater proportion of water than the cryohydrate. As we have seen in §§ 10, 13, where the experiments dealt with brine of NaCl , ice is then formed, and the liquid gets richer and richer in salt, falling in temperature till the ratio proper to the cryohydrate is reached; whereupon, as before, homogeneous solidification ensues without abasement of temperature. If we approach the cryohydrate from this side (that is, by removing ice from a dilute solution), we are sure not to run the risk of being inconvenienced by the intervention of any intermediate hydrate similar to the bihydrate of chloride of sodium (§ 11). But such intermediate hydrates are of the rarest possible occurrence; so that on account of the high specific and latent heat of water, it is invariably most convenient to start from a saturated solution.

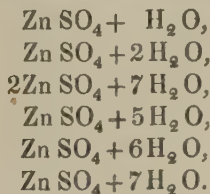
§ 21. *Cryohydrate of Chloride of Ammonium.*—A saturated solution of NH_4Cl was cooled in ice and the liquid portion transferred to a beaker surrounded by an ice-salt freezing-mixture. The temperature fell continuously, and anhydrous chloride of ammonium kept falling down. At -15° the solidifying part presented a different appearance. It then took the form of a brilliant white apparently flocculent mass lighter than the unsolidified liquid. After standing, with stirring, for

a quarter of an hour, the temperature was still -15° . The clear portion was poured off into a fresh beaker, to which the cold was applied. The solidifying parts are now seen to be minute crystals, very much resembling ice-flowers, but opaque. The sides of the beaker become studded with transparent crystals of four sides, which are striated parallel to the sides. By and by these crystals become perfectly white and opaque, and a third axis of crystallization is developed, which was at first suppressed. The crystals are perfectly beautiful, resembling, where opaque, frosted silver. On allowing a thick cup to freeze and breaking it, an exquisite pearly appearance is presented. The structure appears then quite fibrous, the fibres running perpendicular to the axis of the cup; and the appearance, as far as structure is concerned, is similar to that of sublimed chloride of ammonium. The temperature remains constant at -15° C., even to perfect dryness. The first crops of crystals were rejected as being possibly contaminated with NH_4Cl . The last crop and the mother-liquor were analyzed by being weighed into glass basins and evaporated at 100° C.

	grms.	NH_4Cl .	per cent.
I. . .	9.5360	gave 1.7573,	or 18.43
M.L. II. . .	6.0890	,, 1.1895	,, 19.56

The analysis II., which is of the mother-liquor, corresponds nearly with the molecular relation $\text{NH}_4\text{Cl} + 12\text{H}_2\text{O}$, which requires 19.98 per cent. of NH_4Cl .

§ 22. *Cryohydrate of Sulphate of Zinc*.—The hydrates of sulphate of zinc already known are very numerous. They are :—

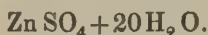


The last, which is the ordinary form of zinc-vitriol, when saturating water at $17^{\circ}.5$ C., gives a solution, according to Karsten, consisting of 52 per cent. of salt and 48 per cent. of water. On cooling such a solution to and below 0° C., the heptahydrate crystallizes out; and this, consisting of 56 of salt to 44 of water,

impoverishes the mother-liquor until the latter contains 30·84 per cent. of the anhydrous sulphate. The temperature is now $-7^{\circ}\text{C}.$, and it remains constant at this degree. The last fraction having solidified at this temperature, was remelted and the water estimated by evaporation and heating to $240^{\circ}\text{C}.$

8·1531 grms. contained 2·5146 grms. of ZnSO_4 ,
or 30·84 per cent.

This corresponds very closely with the composition



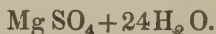
It is noteworthy that this cryohydrate, after standing some days in a hermetically sealed tube, deposits massive rhombic crystals and a fine powder. I have not analyzed these; they are possibly the monohydrate and one of the intermediate hydrates insoluble in the fused cryohydrate.

§ 23. *Cryohydrate of Sulphate of Magnesium.*—Combinations are known consisting of 1 molecule of sulphate of magnesium combined with 1, 2, 6, 7, and 12 molecules of water. The last is the more interesting because Fritsche describes its formation from a saturated solution of the sulphate when cooled below $0^{\circ}\text{C}.$ I find that when a saturated solution is cooled to $-5^{\circ}\text{C}.$ and transferred to a clean vessel, it may, if perfectly free from crystals of the 7-hydrate, be cooled to $-10^{\circ}\text{C}.$ without any further solidification. As soon, however, as further cold causes crystallization, the temperature rises to $-6^{\circ}\text{C}.$, and remains constant at this point during the whole of the subsequent solidification, provided that a crystal of the previous crop is put into the cooled mother-liquor after each decantation.

The composition was determined by heating to $240^{\circ}\text{C}.$

7·6564 grms. gave 1·6736 grm. of anhydrous sulphate,
or 21·86 per cent.

This corresponds to 23·83 (say 24) molecules of water. Its molecular ratio seems therefore to be

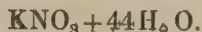


§ 24. *Cryohydrate of Nitrate of Potassium.*—As far as I can inform myself, nitre, like the chloride of ammonium, has not hitherto been combined with water. The solution saturated at $20^{\circ}\text{C}.$ gives an abundant crop of nitre at $0^{\circ}\text{C}.$ There appears

to be no intermediate hydrate, the body which separates at $-2^{\circ}5$ C. being apparently pure nitre. At $-2^{\circ}7$ another body is formed, whose crystalline form resembles ice. It adheres to the side of the vessel; when separated, it floats, being lighter than the mother-liquor at $-2^{\circ}7$; but when thrown into water at 20° C., it sinks, showing that it is not ice. The last four crops of crystals were analyzed. The final one was formed also exactly at $-2^{\circ}7$.

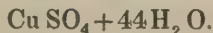
	Liquid.	KNO ₃ .	per cent.
(1)	8.8030	gave 0.9221	or 10.4
(2)	1.6709	„ 0.1959	„ 11.7
(3)	3.0300	„ 0.3350	„ 11.06
(4)	4.2280	„ 0.4770	„ 11.2

The molecular relation is therefore about 1 : 44.6.



§ 25. *Cryohydrate of Sulphate of Copper*.—The ordinary hydrates of blue vitriol are the mono-, bi-, and pentahydrates. On cooling a saturated solution, the constant temperature of solidification is found to be -2° C. The last crop of crystals being remelted, was evaporated and heated to the anhydrous state.

6.6952 grms. gave 1.1312 grm. CuSO_4 , or 16.89 per cent. This corresponds to the atomic relation of 1 : 43.7 (say 1 to 44)



Each crop of crystals, when melted, and the mother-liquor present identically the same depth of colour.

§ 26. *Cryohydrate of Sulphate of Sodium*.—A very great many ordinary hydrates of this salt are known. I find that a saturated solution has a solidifying-point at $-0^{\circ}7$ C.

4.0630 grms. contained 1.850 grm. of Na_2SO_4 ,
or 4.55 per cent.,

corresponding to the molecular ratio of 1 : 165.6 (say 1 to 166),
 $\text{Na}_2\text{SO}_4 + 166\text{H}_2\text{O}.$

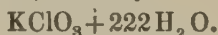
§ 27. *Cryohydrate of Chlorate of Potassium*.—The chlorate of potassium, like the nitrate, has not hitherto been combined with water. Almost the whole of the salt separates out in the anhydrous state when a saturated solution is cooled to 0° C. On further cooling to -3° C., the solution may present a remarkable condition of double supersaturation. If at

this temperature a crystal of anhydrous chlorate is dropped in, anhydrous chlorate is formed in considerable quantity. If an ice fragment is introduced, ice only is formed. If both are thrown in, both are formed, the one set of crystals floating, the other sinking. If the temperature of the supersaturated solution be further cooled, the proper cryohydrate separates out and the temperature rises to $-0^{\circ}5$. The normal formation ensues on introducing a crystal of the cryohydrate from one crop to start the formation of the next. This phenomenon, which is not without its counterpart in some other cases, argues forcibly for the existence of a distinct crystalline form proper to the cryohydrate.

(1) 13.2512 grms. of cryohydrate gave 0.3912 gm. KClO_3 , or 2.95 per cent.

(2) 13.5810 grms. of cryohydrate gave 0.3915 gm. KClO_3 , or 2.88 per cent.

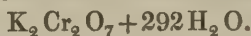
The molecular relation is exactly



§ 28. *Cryohydrate of Bichromate of Potassium*.—I chose this salt because it is not constructed on the ordinary salt type. I found it solidified entirely at -1°C . The crystals, which are at first transparent, become opaque, and are of a bright straw-yellow.

5.4968 grms. gave 0.2868 $\text{K}_2\text{Cr}_2\text{O}_7$, or 5.305 per cent.

This gives the largest ratio of water, namely



As with the sulphate of copper, so in this case all crops of crystals, when melted, had exactly the same depth of colour.

§ 29. *Sources of error*.—I need scarcely point out that the molecular ratios derived from the above experiments can only be considered provisional. In the case of bodies which combine with as many as forty and upwards molecules of water, a very slight error in the determination may make a difference of one or two molecules of water. In those which have a very low solidifying-point, another source of error creeps in. The liquids, even on pouring from one vessel to another, dilute themselves by condensing moisture from the air. With due regard to the probable direction of error in each case, I venture to submit the following tabulation, showing in column 1 the anhydrous salt,

in 2 the temperature Centigrade of solidification, in 3 the actual percentage of anhydrous salt found, and in 4 the number of molecules of water to one of salt.

TABLE VIII.

Temperature of Solidification and Molecular Ratio of Cryohydrates.

(1)	(2) Temp. Cent.	(3) Per cent. of salt.	(4) Molecules of water to 1 of salt.
NaCl	-23 ⁰	23.603	10.5(? 10)
NH ₄ Cl	-15	19.56	12.0
ZnSO ₄	-7	30.84	20.0
MgSO ₄	-6	21.86	24.0
KNO ₃	-2.7	11.20	44.0
CuSO ₄	-2	16.89	44.0
Na ₂ SO ₄	-0.7	4.55	166.0
KClO ₃	-0.5	2.93	222.0
(K ₂ Cr ₂ O ₇	-1.0	5.306	292.0)

§ 30. The above are arranged according to the molecular ratio, NaCl having the least number of molecules of water. At once an important law declares itself: those cryohydrates which have the lowest solidifying temperatures have the fewest molecules of water. This law holds true with all which have been examined, with the exception of the bichromate of potassium, which, if placed according to its temperature of solidification, would be above the sulphate of sodium. Is this due to its abnormal composition? Such questions suggest themselves by the score on contemplating this Table VIII.

§ 31. I have found the solidifying-points, and have hermetically sealed specimens, of the cryohydrates of a few other salts, and am collecting more previous to analyzing them. I give their solidifying-points in the order of the degree of cold; and it will be of great interest to see whether their molecular ratios fall in accord with the above rule.

Salt.	Solidifying temperature of cryohydrate.
KI	-23.0
KBr	-13.0
KCl	-11.4
Na ₂ CO ₃	- 2.0
Ba NO ₃	- 0.8
H ₂ C ₂ O ₄	- 0.5

Perhaps the most promising direction of inquiry for the establishment of such a uniformity of result as may be used for the prediction of untried experiments will consist in a careful study of the nine salts between K, Na, and NH₄ on the one hand, and Cl, Br, and I on the other.

Some Experiments with Sea-water.

§ 32. *Freezing sea-water.*—The sea-water with which the following experiments were performed was procured from Dover. After filtration, it was found to have at 760 millims. the boiling-point 100°·6, while the temperature of its vapour was 100°·2. This sea-water began to freeze at -2° C. On evaporation on a water-bath and keeping at 100° C. for two hours, the percentage of solid residue was 6.5786. A large beaker of this sea-water was cooled to 0° C. A tin vessel was supported inside the beaker so that its bottom just touched the surface of the water; and a freezing-mixture was placed in the tin vessel. When about $\frac{1}{100}$ of the whole had solidified, the solid was removed and divided into two parts: one was allowed to melt, and its percentage of solid matter was determined as above; the other was broken up and frequently pressed between linen and flannel in a screw press, being allowed to melt as little as possible. The percentage of solid matter in this also was determined. The following numbers show the result of this examination:—

	Per cent. at 100° of solid residue.
Sea-water	6.5786
Frozen sea-water	5.4209
Frozen and pressed sea-water	0.4925

It appears, then, that under these conditions the freezing of sea-water is little more than the freezing of ice, and that the

almost undiminished saltness of the unpressed ice is due, as suggested by Dr. Rae, to the entanglement amidst the ice-crystals of a brine richer in solid constituents than the original water itself. Such brine, which is here squeezed out in the press, drains in nature down from the upper surface of the ice-floe by gravitation, and also is replaced by osmic action by new sea-water which again yields up fresh ice; so that while new floes are porous and salt, old ones are more compact and much fresher, as the traveller observed.

§ 33. But, bearing in mind the existence of the cryohydrates, certainly of sulphate of magnesium and doubtless also of chloride of calcium at temperatures below 0° C., a rapid fall of temperature may be accompanied by more complex phenomena of gelation; for if the ice be quickly removed from a large mass of water by freezing, the resulting brine may easily be so enriched as to throw out one or more cryohydrates, which thus perpetuate *in situ* a definite amount of saline matter. How far such cryohydrates are soluble in the chief cryohydrate, namely that of NaCl, which by itself resists the cold so long, is an important matter for future research. But there can even, viewed in the light of the experiments given above, be little doubt that the degree of saltness of a floe depends not only upon its age, but also upon the rapidity with which it was at first formed, and upon the lowest temperature to which it has subsequently been exposed.

§ 34. Since sea-water has no maximum density below its freezing-point, when a mass of sea-water is uniformly cooled to -2° C. ice will be formed at any point, whether at the bottom or at the surface, which loses more heat. Even the middle of a mass of sea-water may lose heat by radiation, and crystals of ice be thus formed in the mass. Or the bottom of the sea may radiate sufficient heat through the ice-cold layers above to freeze the water in contact with it, and thus generate large masses of ice which break off and carry with them parts of the sea-bottom. But I suppose the ice of the sea is mainly formed at or near the surface by radiation from the surface into space and by contact with the colder air. To imitate as nearly as I could the condition which I suppose to exist, I cooled the sea-water to -2° C. in a beaker, which I enveloped thickly with flannel. I tried in vain to freeze the surface by

blowing over it dry air which had passed immediately before through a long pewter worm immersed in a freezing-mixture. But I succeeded in getting a sheet of ice when I hung a freezing-mixture contained in a blackened tin pan within about $\frac{1}{8}$ inch of the surface of the water, the whole being plentifully enveloped in flannel. Perhaps here the actual conditions which obtain when sea-water freezes were reproduced. I found that the pressed ice contained only 0.4052 of solid residue at 100° C.

§ 35. The question suggested itself to me whether, when one part of a solution of a salt is cooled, there may not be an accumulation of salt in the cooler part, although not accompanied by any solid separation. I accordingly cooled a saturated solution of nitre to -1° C. and decanted from the separated nitre. I then warmed the solution in a tall beaker-glass to 60° C. and placed the bottom of the beaker in melting ice. In an hour's time a thermometer at the bottom stood at 10° C., at the top at 33° . A specimen from the bottom contained 11.3 per cent. of nitre; one from the top contained 11.7 per cent. of nitre—showing that there was no sensible diffusion of the salt one way or the other.

General Considerations.

§ 36. *Maximum density of Water.*—It was shown that brines of various strength, when mixed with water, absorbed heat and expanded. Let us look upon ice as the cryohydrate of water. Water shrinks as it loses heat till it reaches 4° C. At this point ice is formed, which, however, is dissolved in the water. A solution is obtained having a temperature of solidification below 4° C., namely at 0° C. At 0° C. the ice and the water solidify together, producing the compound body or cryohydrate called ice, which is thus a cryohydrate of water. The expansion from 4° to 0° is due to the greater and greater amount of ice which the water holds in solution, and which expansion is greater than the contraction of the water due to the diminished temperature.

§ 37. *Variation of media.*—There can be no doubt that the discovery of an enormous number of new bodies of definite composition will reward those who labour in this field. Taking water as the medium for solution, there appears to be no doubt that every soluble salt has a definite cryohydrate; so that in this

direction alone the number of new bodies awaiting discovery and description may be estimated at half the number of bodies already known. If we vary the medium, employing, say, alcohols or hydrocarbons as solvents, the number of new compounds will be again indefinitely increased; so that it is fairly within the truth to assert that the number of known bodies may soon be doubled.

§ 38. *Geological*.—The behaviour of mixtures of salts will again offer a new chapter for study; and I suppose we may expect that much light will be thus thrown upon some of the most obscure geological questions. For though we have been considering above cryohydrates (that is, compounds of water solidifying below the freezing-point of water), there can be no discontinuity separating the medium water with its peculiar temperature of solidification from other media of very different melting-points. We know already, indeed, very many instances in which the mixture of two bodies has a lower melting-point than either of its constituents. What must happen, then, if a mass of molten rock, such as a silicate, is saturated at a high temperature with another silicate? When the mixture cools, the second may separate out in the solid form, perhaps as quartz, perhaps as felspar, or what not. Anon, at a certain lower temperature, solidification takes place between the medium and the dissolved rock in definite proportion—definite, though perhaps not necessarily in chemical ratio, but presenting that mineralogical ratio which is so striking, and which has not hitherto been satisfactorily explained.

§ 39. *Constant temperatures*.—Perhaps one of the most interesting aspects of the experimental results is the establishment of fixed temperatures below zero. With the exception of the melting-points of a few organic bodies such as benzol, and the boiling-points of a few liquids such as liquid ammonia, sulphurous acid, and carbonic acid, and the rather ill-defined temperatures to be got by various freezing-mixtures, there are no means in the hands of physicists for obtaining and maintaining with certainty and ease a fixed temperature below 0°C . Now, if we surround a body with one of the solid cryohydrates described above, the body is kept at a corresponding temperature as long as any of the cryohydrate remains solid, and this with as much certainty as the temperature 0°C . can be main-

tained by melting ice. We thus command temperatures between -23° and 0° C. with the greatest precision.

§ 40. *Invitation to others.*—I need scarcely point out that the field of inquiry which has been here opened is far too large to be satisfactorily examined by one worker. It is notably at the commencement that the collaboration of many workers is most beneficial, so that fundamental errors may be quickly corrected. On this ground I respectfully invite my fellow-labourers to this branch of inquiry.

I have received through a considerable part of this inquiry much valuable assistance from my friend Mr. F. H. Marshall.

January 18, 1875.

XII. *On Salt Solutions and Attached Water.*

By FREDERICK GUTHRIE.

II.

Cryogens and Cryohydrates.

By Cryogen I mean an appliance for obtaining a temperature below 0° C. In this paper it always signifies a freezing-mixture. By Cryohydrate I mean the body resulting from the union of water with another body, and which hydrate can only exist in the solid form below 0° C. As this communication is in every respect continuous with the one brought before the Physical Society on November 7th, 1874, and published in the Philosophical Magazine for January 1875, the paragraphs are numbered in sequence with those of the previous communication.

CRYOGENS.

Precision of Temperature of Freezing-mixtures.

§ 41. In § 39, when I was speaking of the possible uses of cryohydrates for the maintenance of constant temperatures, I said:—"With the exception of the melting-points of a few organic bodies such as benzol, and the boiling-points of a few liquids such as liquid ammonia, sulphurous acid, and carbonic acid, and the rather ill-defined temperatures to be got by various

freezing-mixtures, there are no means in the hands of physicists for obtaining and maintaining with certainty and ease a fixed temperature below 0°C. "

In regard to freezing-mixtures, I confess to have been here very much misled by the confident but rather erroneous statements of others, to which I attached faith trebly blind—blind, because no recorded experiments really support them, blinder still because a little thought in the right direction must have shown their fallacy, and blindest of all because the one experiment of my own in this direction (§§ 16 and 17) shows that the minimum temperature of an ice-salt cryogen is reached whether we take the ratios 3 of salt to 1 of ice or 1 of salt to 2 of ice, and so points to the wideness of the margin of ratio which may obtain between the weights of ice and the salt. It will further be shown in §§ 44–46 that the temperature of the constituents has nothing to do with the temperature reached, and in § 49 that the degree of hydration of the salt employed is often without effect.

Accordingly I unqualifiedly withdraw the expression "ill-defined" as applied to freezing-mixtures. They may be, on the contrary, bodies of precise temperature under widely varying circumstances.

§ 42. The enormous latent heat of water, the fact that the specific heat of ice is only about half that of water, while the specific heats of all salts are far less than that of ice, and therefore, *à fortiori*, less than that of water, together with the good thermal conductivity of water, all argue that, if constantly stirred, all parts of a freezing-mixture will have the same temperature. The fact that the liquid portion of a freezing-mixture of ice and a solid salt is the cryohydrate of that salt, ensures the identity of the resulting temperature under various conditions of proportion. The constant tendency to the formation of this cryohydrate by contact between the solids is always seeking to depress the temperature; while the solidification of the cryohydrate at an indefinitely small fraction of a degree below the temperature of the freezing-mixture, and the consequent liberation of heat, ensures the temperature against such fall.

Statements therefore, whether previously made by myself or others, that it is advantageous to weigh the salt and ice in definite proportion, that the ice should be dry, that snow is preferable to ice on account of its state of finer division, that additional cold

is produced by previously cooling the ice or salt or both, are to be put aside as untrue—untrue, that is, as far as the temperature or heat-tension is concerned. To obtain the greatest quantity of heat-absorption with a given amount of salt, such a quantity of ice must be taken as will form with the salt a cryohydrate. The proportions can be at once gathered from Table X. § 90.

§ 43. Further, the fact that all cryohydrates, with, I believe at present, the sole exception of sulphate of zinc and chloride of magnesium, have far more water than that ordinary hydrate which has most water, shows that it cannot matter whether a salt which affects water of crystallization be employed in the anhydrous state or with its crystalline water.

It may, however, be otherwise with salts containing the elements of water more intimately associated; and, as we shall see in one case at least, an anhydrous compound may melt ice with which it is in contact and heat the so-formed water far above zero, while the compound so formed, when cool, will when mixed with a fresh quantity of ice absorb heat abundantly. I suppose in such cases double decomposition ensues; and though nothing is eliminated, there is a rearrangement of the elements more intestinal than that effected by the association with water.

§ 44. *Effect of the Temperature of the Ingredients on that of the Freezing-mixture.*—An ounce of finely powdered chloride of sodium was cooled in a flask surrounded by a freezing-mixture till its temperature was -15° C. It was then stirred with four ounces of ice, which had been cooled and had the temperature -10° . As soon as liquefaction began, the temperature -22° was reached; and this degree of cold was never surpassed.

§ 45. The same degree of cold (-22°) resulted from the mixture of 1 oz. of NaCl at -15° with 4 oz. of ice at 0° , also when 1 oz. of salt at $+12^{\circ}$ C. was mixed with 4 oz. of ice at -12° C.

§ 46. Indeed the margin of temperature may be greatly extended. Thus, 1 oz. of NaCl in powder was heated to incipient redness and thrown upon 5 or 6 oz. of ice at 0° ; after a few minutes constant stirring, the temperature had reached -22° .

§ 47. 1 oz. of dry anhydrous Na_2SO_4 was heated nearly to redness, and thrown upon 4 oz. of ice at 0° . In a few minutes the temperature had sunk to $-0^{\circ}7$. Again, an ounce of anhydrous CuSO_4 was heated to about 600° C., and thrown upon

4 oz. of ice; the temperature at once sank to $-0^{\circ}5$ (compare § 55).

§ 48. From the above experiments, and from the theoretical considerations touched upon in § 42, I conclude that, within very wide limits as to quantity, the temperature of a freezing-mixture may be very independent of the temperature both of the salt and of the ice.

§ 49. *Effect of Crystalline Water in the salt on the Temperature of the Freezing-mixture*—From § 26 it appears that crystallized sulphate of soda ($\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$) gives with ice a temperature of $-0^{\circ}7$. Deprived of water, the anhydrous salt N_2SO_4 gave with ice the temperature also of $-0^{\circ}7$. Sulphate of copper in the anhydrous state produced, when mixed with ice, a temperature of $-1^{\circ}7$, while with the ordinary crystallized hydrate the temperature was -2° .

§ 50. Having examined six or seven other salts as to the temperature of their freezing-mixtures when employed both with and without their crystalline water, I do not scruple to assert that water of crystallization, properly so called, takes no effect upon the temperature of the freezing-mixture; and I believe the same is true of that water which has been called constitutional. But where a profound rearrangement of the elements of water ensues, the effect may be different, as appears in the next paragraph.

§ 51. The chloride of aluminium, AlCl_3 , as offered in commerce, fumes strongly in the moist air, so great is its avidity for water. Thrown upon several times its own weight of ice, the two liquefy and the temperature stands above 0° . The strongest commercial solution of chloride of aluminium, however, when at the temperature of the air or at 0° or at 100°C ., will reduce the temperature to -13° when poured upon three or four times its own weight of ice. I suppose the anhydrous chloride may be viewed as separating the atoms of the water-molecule, as is supposed to be the case with the chlorides of phosphorus.

§ 52. *Hydrochloric Acid as a Cryogen with Ice*.—Ordinary commercial hydrochloric acid when poured upon ice may produce as much as 22° of cold. The amount of HCl in the hydrochloric acid, however, is here to be as much considered as it would have to be if we dealt with ice and a solution of NaCl . In the experiments which are given in the succeeding paragraphs as far as § 54, the hydrochloric acid employed was formed by saturating

water with the gas, while the liquid was kept after absorption had ceased for half an hour at 0° while the acid passed through. The barometric pressure was 770 millims. This may be considered a normal acid.

§ 53. The acid at 0° was poured in various proportions upon ice at 0° . Fifty grms. of ice were used in each experiment. The Table shows within what small limits of ratio the minimum temperature is reached. In the Table the weight of the ice is taken as unity.

Weight of ice at 0° C.	Weight of $\text{HCl} + n\text{H}_2\text{O}$ at 0° C.	Resulting Temperature.
1	1.5	-3°
1	0.4	-26
1	0.3	-23
1	0.2	-19

We are therefore, when dealing with a cryogen one of whose constituents is a liquid, much more limited in the range of ratio which we may employ to procure the maximum cold than is the case when both are solid.

§ 54. Accordingly, in examining the effect of the alteration in the temperature of one or both of the constituents, it is necessary always to use the same ratio. In the Table below, the ratio used was that which gave the maximum cold when both were at 0° C., namely 1 of ice to 0.4 of the saturated solution of HCl. It must be understood that in those cases where the hydrochloric solution was used below 0° C., it is not meant that the saturation with HCl took place at that lower temperature, but that, having been saturated at 0° , the solution was subsequently cooled to the lower temperature.

1 ice at -15°	with 0.4 HCl sol. at 0°	gave -28° .
1 " 0°	" 0.4 " "	-15° " -27° .
1 " -15°	" 0.4 " "	-12° " -27° .

All these numbers are sufficiently near to -26° , the number got when both ingredients are at 0° , to justify the conclusion that the temperature of the ice has something, but little, to do with the temperature of the freezing-mixture. And it appears that the temperature of the HCl solution is also without effect, provided that the saturation has been effected at the same temperature and pressure. The water acts, indeed, here much as the water of crystallization acts in the case of solid salts.

§ 55. *Table of Freezing-mixtures.*—In the following Table the lowest attainable temperature is given. This, as we have seen, is independent of the temperature of the salt and its degree of crystalhydration. The temperatures are got on mixing the salt with three to six times its weight of ice in lumps of the size of a pea downwards. The salts are arranged according to the degree of cold they furnished.

TABLE IX.—Freezing-mixtures.

	° C.		° C.
NaBr	−28·0	KCl	−10·5
NH ₄ I	{ 27·0	K ₂ CrO ₄	10·2
		BaCl ₂ +2H ₂ O	7·2
NaI	26·5	Sr2NO ₃	6·0
CuCl ₂	24·5	MgSO ₄ +7H ₂ O	5·3
KI	22·0	ZnSO ₄ +7H ₂ O	5 0
NaCl	22·0	KNO ₃	3·0
MgCl ₂ +6H ₂ O	20·5	Na ₂ CO ₃	2·2
SrCl ₂ +6H ₂ O	18·0	CuSO ₄ +5H ₂ O	2·0
2NH ₄ , SO ₄	17·5	FeSO ₄ +7H ₂ O	1·7
NH ₄ Br	17·0	K ₂ SO ₄	1·5
NH ₄ NO ₃	17·0	K ₂ Cr ₂ O ₇	1·0
NaNO ₃	16·0	Ba2NO ₃	0·9
NH ₄ Cl	16·0	Na ₂ SO ₄ +10H ₂ O	0·7
FeCl ₃ (commercial)	16·0	KClO ₃	0·7
Ca2NO ₃ +4H ₂ O	14·0	AlNH ₄ 2SO ₄ +12H ₂ O	0·4
KBr	13·0	HgCl ₂	0·2
AlCl ₃ in strong sol.	13·0	NH ₄ CO ₂	0·2

We shall study this Table in connexion with the temperature and molecular ratios of the cryohydrates of the same salt.

CRYOHYDRATES.

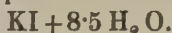
Cryohydrates of the Halogen Alkalies.

§ 56. As was anticipated in § 31, the study of the nine salts resulting from the union of the halogens with the alkali metals has brought to light many points of interest. The two members of this family which I had previously examined were NaCl, solidifying at −23° with 10·5 molecules of water, and NH₄Cl, solidifying at −16° with 12 molecules of water. I have reexamined the cryohydrate of chloride of ammonium; and the mean

of several analyses gives 19·27 per cent of chloride, which brings the ratio to $\text{NH}_4\text{Cl} + 12\cdot4\text{H}_2\text{O}$.

There is nothing particular to remark in the analysis of this group. All, excepting the ammonium salts, bear heating to 300° or 400°C . without decomposition or volatilization. The liquid cryohydrates were weighed in covered basins of Bohemian glass, evaporated to dryness, strongly heated, covered, and quickly cooled. The ammonium salts were heated on the water-bath till they ceased to lose weight.

§ 57. *Iodide of Potassium*.—This salt, which at the ordinary temperature is so abundantly soluble in water, yields a large proportion of anhydrous salt when cooled. An ice-salt cryogen fails to solidify it, but just brings it to the verge of solidification, removing all the free salt in the same manner as it does with NaCl solution, excepting that there does not appear to be any intermediate cryohydrate corresponding with $\text{NaCl} + 2\text{H}_2\text{O}$. The KI solution appears to be homogeneous at -8° or -12° . When subjected to solid CO_2 and ether, it at once begins to solidify at -22° to -23° , and retains this temperature to dryness. Of the four parts into which the substance was divided as it solidified, two were analyzed—namely, the second crop of crystals, and the finally solidified and remelted mother-liquor. Of the first, 5·8240 grms. gave 3·0120 anhydrous KI , or 51·72 per cent.; of the second, 6·3960 grms. gave 3·331, or 52·07 per cent. The latter corresponds to the molecular ratio



§ 58. *Bromide of Potassium*.—This forms a cryohydrate of great beauty. At -13° the characteristic crystals are seen to be produced. They have the fern-like shape of ice-crystals. The fronds are studded with a fructification of opaque crystals, whose opacity seems to spread through the at first transparent fronds till the whole resembles frosted silver. The two portions which were taken for analysis were the final part, or that which solidified last, and the immediately preceding crop of crystals. Of the former, 7·8285 grms. gave 2·5170 of KBr ; of the latter, 9·4560 grms. gave 3·0070 dry salt. These correspond respectively with 32·15 and 31·80 per cent. The first points to the molecular relationship



§ 59. *Chloride of Potassium*.—Since KI is thus seen to com-

bine with 8·5 of water and KBr with 14 of water, the one a fraction and the other a whole number, I spared no care in the preparation and analysis of the chloride of potassium, to see whether the fractional relationship did not arise from experimental error. Perfectly pure K_2CO_3 was dissolved in a slight excess of HCl, evaporated to dryness, and ignited in a platinum basin. The KCl was recrystallized four times. Six ounces of the saturated solution were cooled; solid matter separated down to -10° . At this temperature the separated salt appeared as a cloudiness in the liquid, a little heavier than the latter, and of a granular but translucent appearance. The liquid may now be cooled to -15° ; but it is now a supersaturated solution of the true cryohydrate—a solution, it is to be observed, of which the solid crystals present are unable to determine the solidification. At a little below -15° , long ice-like crystals shoot out and the temperature rises to $-11^\circ\cdot4$, which is the crystallizing-point of the cryohydrate. From this behaviour I am disposed to admit that there may be an intermediate hydrate similar to the bihydrate of NaCl.

Of the last portion which solidified, 6·588 grms. gave 1·320 of anhydrous salt. Of the previous crop of crystals 7·869 grms. gave 1·579 of salt. These show the respective percentages 20·03 and 20·07, both of which point to the relationship



§ 60. The halogen salts of potassium arrange themselves according to the cold required for the solidification of their cryohydrates, and according to the molecular ratio of water, as follows:—

	Solidifying-temperature of cryohydrate.	Number of molecules of water to 1 of salt.
KI . . .	-23	8·5
KBr . . .	-13	14·0
KCl . . .	$-11\cdot4$	16·5

We find here the general rule confirmed, that among like salts the lower the temperature of solidification of the cryohydrate, the smaller is the number of molecules of water which it contains.

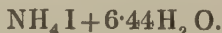
§ 61. *Iodide of Ammonium*.—This salt gave me considerable

trouble. It is difficult to obtain in perfectly colourless crystals; and both the solid and its solution are disposed to change colour, becoming brown when kept, even in the dark. Heating in a water-bath with constant stirring restores the dry altered salt to a light-grey colour. Analysis showed that this coloration did not sensibly affect the percentage composition of the salt; but still its power of assuming water might be seriously affected. A saturated solution was exposed for some hours to an ice-salt cryogen at -22° ; it was then exposed to the carbonic-acid-and-ether cyanogen. It solidified wholly at from -27° to -28° . While solidification is taking place, the cryohydrate is nearly perfectly white. When dry and over-cooled, it assumed a pinkish grey colour, resembling chloride of silver which is beginning to be affected by light.

The analysis of these portions is given, namely:—(1) the last to solidify or remelted mother-liquor; (2) the immediately preceding crop of crystals; and (3) the crop before (2). As the results are by no means in good accord, I give them all:—

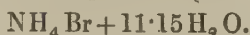
	Solution.	NH_4I .	per cent.
(1)	5.2935	gave 2.9375, or	55.49
(2)	5.4960	„ 3.2120, „	58.42
(3)	8.4560	„ 4.8675, „	57.56

The portion (1), which, being the last, is in one sense likely to be the most homogeneous, corresponds to the relationship



The portions (2) and (3) would indicate as much as 0.7 molecule less of water.

§ 62. *Bromide of Ammonium*.—This salt separates as a cryohydrate from a saturated solution at -17°C . Its formation is well marked, and its analysis was satisfactory. Of the final portion, 4.2591 grms. gave 1.3680 of NH_4Br . Of the immediately preceding crop of crystals, 5.5990 grms. gave 1.8010 of NH_4Br . The percentages are 32.12 and 32.17 respectively: these numbers correspond to the relationship

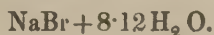


§ 63. Taking the value of the cryohydrate of chloride of ammonium from § 56 as $\text{NH}_4\text{Cl} + 12.4\text{H}_2\text{O}$, we have for the halogen salts of ammonium:—

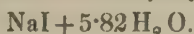
	Solidifying-temperature of cryohydrate.	Number of molecules of water to 1 of salt.
NH ₄ I . . .	-27.5	6.4
NH ₄ Br . . .	-17	11.1
NH ₄ Cl . . .	-16	12.4

whence it is gathered that the relative faculties of chlorine, bromine, and iodine, in depressing the temperature at which the cryohydrates are formed, are similar with ammonium to their faculties with potassium; namely, with both, iodine gives a lower-solidifying cryohydrate than bromine, and bromine lower than chlorine; and we have here also confirmation of the rule that in the same series the aquavalents diminish with the temperature of solidification.

§ 64. *Bromide of Sodium*.—To complete this series I take now the halides of sodium. The bromide of sodium separates from a saturated solution as a cryohydrate at -24° C. Taking the last and the next to the last portions, 7.5010 grms. of the former gave 3.1000 of anhydrous bromide; of the latter, 8.3160 grms. gave 3.4605 of NaBr. The corresponding percentages are 41.33 and 41.61, the first of which indicates 8.12 and the second 8.08 molecules of water to 1 of the salt.



§ 65. *Iodide of Sodium*.—A saturated solution of iodide of sodium presents in the most remarkable manner the phenomenon of supersaturation. It may be cooled to -22° , freely exposed to the air, and shaken without solidifying. On being placed in contact with solid carbonic acid and ether, it solidifies, and its temperature instantly rises to -15° . The solidification once started by this extreme cold, the temperature remains constant at -15° . Fragments of the cryohydrate so formed induce solidification in other portions subjected to the ice-salt cryogen. The last two portions were analyzed. Of the very last, 6.4000 grms. gave 3.8050 of NaI, or 59.45 per cent. Of the next to the last, 10.2450 grms. gave 6.0845, or 59.39 per cent. The molecular ratio of the cryohydrate is accordingly



Correlating the iodide and bromide of sodium with the chloride, we have, therefore,

	Solidifying-temperature of cryohydrate.	Number of molecules of water to 1 of salt.
NaI . . .	-15	5·82
NaBr . . .	-24	8·12
NaCl . . .	-23	10·5

§ 66. It appears that the iodide of sodium forms the first exception we have yet met with to the general rule; for while its solidifying-point is above that of its companions, it attaches to itself a less number of water-molecules. In the Table below the whole nine combinations are shown; and they are there arranged according to the number of molecules of attached water, or in what might be called their "aquavalents" if this expression were not too symphonous with "equivalents." Say, therefore, "water-worths."

Salt.	Temperature of solidification of cryohydrate.	Water-worth.
NaI	-15	5·8
NH ₄ I	-27	6·4
NaBr	-24	8·2
KI	-23	8·5
NaCl	-23	10·5
NH ₄ Br	-17	11·1
NH ₄ Cl	-16	12·4
KBr	-13	14·0
KCl	-11·4	16·5

It appears that, for the same halogen, a sodium salt attaches less water than an ammonium salt, and the ammonium salt less than the potassium salt. Also, for the same metal, an iodine salt attaches less water than the bromine salt, and the latter less than the chlorine salt.

Or if we denote by ${}^w\text{X}$ the number of molecules of water attached to one molecule of XM , then

$${}^w\text{X Na} < {}^w\text{X NH}_4 < {}^w\text{X K},$$

and

$${}^w\text{IM} < {}^w\text{BrM} < {}^w\text{ClM}.$$

This remarkable rule has no exception amongst the above nine salts; and the only exception to the general rule, that the lower

the solidifying-point the fewer the molecules of associated water, is offered by the iodide of sodium. Concerning this see § 68.

§ 67. It may be perhaps more than accidental that the numbers of molecular water-worths show a distinct tendency to be multiples of 0.5. For my own part, recognizing the possible range of analytical error, I for the present distinctly forbear to express any opinion as to whether we are here dealing with the same physical force which constitutes chemical attraction; and which regulates the integral ratios of molecular combination as most chemists appear to understand the term—or whether it is a distinct or distinctly conditioned force binding the salt and water together in quite a new ratio, or a ratio which can only be brought to the chemical one by multiplication by constants, at present arbitrary.

It is useful, however, to reflect that almost innumerable instances are known in which the molecular ratio between a salt and its ordinary water of crystallization is not a simple one. On examining the published determinations of water of crystallization effected by the chemists who are or have been both accurate and scrupulous, we find that in many cases a less simple numerical ratio between the salt and its water would often correspond with the derived result far better than the ratio which has been thence deduced.

§ 68. With regard to the solidifying-point of the cryohydrate of iodide of sodium, I may here at once mention the exceedingly interesting fact which will be discussed in its proper place, that while the cold of a cryogen formed by mixing with ice any one of the other of these eight salts is so closely near as to be considered identical with the solidifying point of the corresponding cryohydrate, the cold of a freezing-mixture consisting of ice and iodide of sodium far exceeds -15° , and in fact reaches -28° , nearly the lowest temperature which I have yet got. On this ground it would be really entitled to be placed at the head of the list of the nine, where its water-worth has placed it in Table (§ 66).

§ 69. *Speculation concerning NaI.*—It is clear that when a freezing-mixture is in action, the liquid portion is a solution of the salt of such a strength that it resists solidification at the temperature of the mixture. Accordingly there must be a cryohydrate of sodium which remains liquid down to -28° . Is its

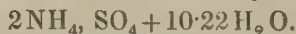
crystalline form so peculiar as not to respond by solidification to any solid particles in the air, and so to be an exceptionally persistent instance of supersaturation? Perhaps the cryohydrate can only exist in the liquid form. When it loses heat, it does not solidify as a whole, but in two parts, each of which is less soluble than the two together. For this reason the mixed solid separated would in all its stages have the same composition as the simple cryohydrate, while its separation, when once begun, might keep itself in activity. The heat-tension then exhibited would be the mean of the temperatures due to the solidification of each constituent.

I can scarcely assert that this is a satisfactory or even to my own mind a clear explanation of the phenomenon. The difficulty would be to some extent removed if we could get evidence of an intermediate cryohydrate resembling that which exists with NaCl. Of such a cryohydrate I have no substantial evidence to offer at present.

Cryohydrates of Alkaline Sulphates.

To see whether the noticeable relation between sodium, ammonium, and potassium is valid in other compounds of these metals, their sulphates were examined.

§ 70. *Sulphate of Ammonium*.—This body, when dissolved to saturation in water, yields abundantly the ordinary hydrated sulphate of ammonium when cooled to 0°C . The separation stops shortly below 0°C .; and the solution may be cooled to -22° while the liquid remains quite clear. This possible depression of the temperature in presence of one hydrate is clearly a happy incident in the genesis of the cryohydrate as far as the assurance of the freedom of the latter from the former is concerned. On cooling by means of carbonic acid and ether, solidification ensues shortly below -22° , and the temperature rises to -17° , at which it remains constant. Of the portion last to solidify, 7.0105 grms. on evaporation to dryness and heating to 130° , gave 2.9280 of $2\text{NH}_4\text{SO}_4$, or 41.7 per cent. Of the immediately preceding portion, 4.0695 grms. gave 1.7195, or 42.0 per cent. The first of these corresponds to the relation



§ 71. *Sulphate of Potassium*.—The saturated solution of this salt solidifies at $-1^{\circ}.2$. Of the last portion, 3.9095 grms.

yielded 0.3075, or 7.8 per cent. of K_2SO_4 . Of the immediately preceding part, 5.2905 grms. gave 0.3960, or 7.5 per cent. The first of these shows the molecular relation



§ 72. *Sulphate of Sodium*.—This was examined in § 26. Its cryohydrate is formed at $-0^{\circ}.7$. The percentage of Na_2SO_4 in the last portion was found to be 4.55, and the water-worth 165.6.

§ 73. Accordingly we have the sulphates of the alkalies arranged as follows:—

	Temperature of solidification of cryohydrate.	Water-worth.
$2NH_4SO_4$. . .	-17°	10.2
K_2SO_4 . . .	-1.2	114.2
Na_2SO_4 . . .	-0.7	165.6

Once more, therefore, the lower the temperature of solidification of the cryohydrate, the less is its water-worth. But the order is different with SO_4 from the order with a halogen.

Nitrates of the Alkalies.

§ 74. *Nitrate of Ammonium*.—The nitrate of ammonium separates as a cryohydrate from a saturated solution at $-17^{\circ}.2$ in exceedingly beautiful fern-like crystals. Dried at $100^{\circ}C$. and heated to incipient fusion, 7.6100 grms. of the part last to solidify gave 3.3265 of the anhydrous salt. Of the next to the last, 7.2755 grms. gave 3.1475. The former therefore contained 43.71 per cent. of NH_4NO_3 , the latter 43.26. The first indicates the relation

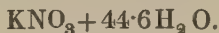


§ 75. *Nitrate of Sodium*.—The temperature at which this cryohydrate is formed was found by experiment to be $-17^{\circ}.5$; but, for reasons partly considered in § 69, I believe this temperature to be too low, and that, when supersaturation does not intervene, the temperature is $-16^{\circ}.5$. Here, however, I assign to it the temperature got by direct observation. Of the last portion to solidify, 5.1210 grms. gave 2.2140 of $NaNO_3$, or 40.8 per cent., which indicates the composition



Of the previous crop of crystals, 6·9820 grms. gave 2·8850 of NaNO_3 .

§ 76. *Nitrate of Potassium*.—This was examined in § 24. The cryohydrate solidifies at $-2^{\circ}\cdot6$, and contains 11·2 per cent. of nitre. The water-worth is expressed by the relation



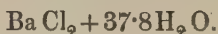
§ 77. The nitrates of the alkalies therefore arrange themselves as follows:—

	Temperature of solidification of cryohydrate.	Water-worth.
NH_4NO_3 . . .	$-17^{\circ}\cdot2$	5·72
NaNO_3 . . .	$-17^{\circ}\cdot5$ (16·5)	8·13
KNO_3 . . .	$-2^{\circ}\cdot6$	44·6

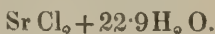
I believe that here again the water-worth really falls with the temperature of solidification. But the order of the salts in regard to their water-worths is again different from the order observed with the sulphate, as well as from that of the chlorides of the same metals.

Chlorides of the Alkaline Earths.

§ 78. *Chloride of Barium*.—The chloride of barium in saturated solution becomes a solid cryohydrate at -8° C. Of the portion last to solidify, 6·6790 grms. gave, on evaporation and heating to 350° C., 1·5490 Ba Cl_2 . This corresponds to 23·2 per cent. Of a previous crop of crystals, 6·1350 grms. gave 1·4735 Ba Cl_2 , or 24·0 per cent. The first of these shows the formula



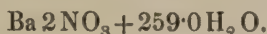
§ 79. *Chloride of Strontium*.—This salt forms a cryohydrate at -17° . Of the final portion, 5·8325 grms. contained 1·6085 of Sr Cl_2 , or 27·57 per cent. The crop before this showed 1·3655 grm. of salt in 4·9675 solution, or 27·5 of Sr Cl_2 . We may therefore deduce the formula



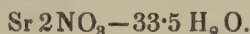
Nitrates of the Alkaline Earths.

§ 80. *Nitrate of Barium*.—The cryohydrate of this salt solidifies from a saturated solution at $-0^{\circ}\cdot8$. I have only one deter-

mination of its composition ; namely, 3·0370 grms. gave 0·1610 of anhydrous salt, which corresponds to 5·30 per cent., and the molecular ratio

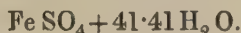


§ 81. *Nitrate of Strontium*.—On cooling a saturated solution to -6° the cryohydrate solidifies. Of the last portion, 6·8010 grms. gave 1·7675, or 25·99 per cent. of Sr 2NO_3 . Of the previous crop of the cryohydrate, 4·6715 grms. contained 1·2105 of the anhydrous salt, or 25·91 per cent. These determinations concur towards the relationship



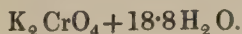
Miscellaneous Cryohydrates.

§ 82. *Sulphate of Iron*.—Green vitriol separates from a saturated solution at $-2^\circ\cdot2$. The next to the last portion of the cryohydrate showed the following composition :—4·7000 grms. gave 0·8155 FeSO_4 , or 17·35 per cent. Of the last portion, 4·8140 grms. gave 0·8155, corresponding to 16·94 per cent., and showing the ratio



Although the solution of this salt was quite clear when hermetically sealed for analysis in a tube containing not more than ·5 cubic centim. of air, a considerable deposit of sesquioxide took place. The analysis, therefore, is probably not quite exact.

§ 83. *Chromate of Potassium*.—The cryohydrate solidifies at -11° . Of the last crop of crystals, 3·0690 grms. gave 1·1145 anhydrous salt, or 36·27 per cent. Of a previous crop, 5·4775 grms. gave 1·9945, or 36·41 per cent. The first indicates the formula

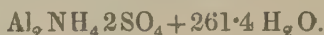


From § 28 the bichromate has a cryohydrate solid at -1° and containing 292 molecules of water. Accordingly

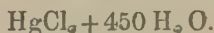
	Temperature of solidification.	Water-worth.
Chromate, $\text{K}_2 \text{Cr O}_4$	. -11°	18·8
Bichromate, $\text{K}_2 \text{Cr}_2 \text{O}_7$	. -1	292·0

§ 84. *Ammonium Alum*.—This body was examined on account of the large percentage of water which is held by the ordinary

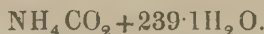
hydrated salt. The cryohydrate solidifies at $-0^{\circ}2$. The part last to solidify was examined; of this, 4.3845 grms. contained 0.2060 gm. of anhydrous alum. This shows 4.7 per cent. Of the immediately preceding crop of crystals, 5.2400 grms. gave 0.2220 of anhydrous alum, or 4.2 per cent. The first of these determinations indicates the relationship



§ 85. *Perchloride of Mercury*.—A saturated solution of corrosive sublimate solidifies at $-0^{\circ}2$. The ultimate and penultimate portions were examined. Of the former, 6.0640 grms. gave 0.197, or 3.24 per cent.; of the latter, 4.977 grms. gave 0.164, or 3.29 per cent. The first indicates the formula



§ 86. *Oxalate of Ammonium*.—This solidifies as a cryohydrate at $-0^{\circ}2$. Of the last portion to solidify, 4.340 grms. contained 0.125, or 2.8 per cent. of the anhydrous salt. This agrees with the relation



§ 87. *Carbonate of Sodium*.—After igniting the carbonate so as to decompose any bicarbonate, the saturated salt solidifies as a cryohydrate at -2° . Of the final portion, 6.4090 grms. contained 0.383 of Na_2CO_3 . This shows 5.97 per cent., or the relation



§ 88. The following Table shows at a glance the relation between the lowest attainable temperature when the salt is mixed with ice, the temperature of the solidification of the cryohydrate, the water-worth or aquavalent. Column 1 shows the salt employed, and the degree of hydration when associated with water of crystallization. Column 2 shows the temperature obtained when the salt is mixed with ice. Column 3 shows the temperature at which the cryohydrate separates. In column 4 are shown the number of molecules of water associated with one molecule of the salt in the cryohydrate. It is here called "water-worth." In column 5 are the percentages of the anhydrous salt which the final portions of the cryohydrates contained, according to the analyses given above. The letters M.L. show that the liquids here analyzed stood before solidification in the

relationship of mother-liquors to the preceding crops of cryohydrate. In column 6 are analyses of the crop of cryohydrate immediately preceding the last cryohydrate. The salts are arranged according to the degree of cold attainable when the salt is used as a cryogen, *i. e.* in a freezing-mixture.

TABLE X.—Showing (1) the chemical formula of the salt, (2) the lowest temperature to be got by mixing the salt with ice, (3) temperature of solidification of the cryohydrate, (4) molecular ratio between anhydrous salt and water of its cryohydrate (water-worth or aquavalent), (5) percentage of anhydrous salt in portion of cryohydrate last to solidify, (6) percentage of anhydrous salt in crop of cryohydrate before the last.

(1) Formula of salt.	(2) Temperature of cryogen.	(3) Temperature of solidification of cryohydrate.	(4) Molecular ratio or water-worth or aquavalent.	(5) Percentage of anhydrous salt in last cryohydrate, M.L.	(6) Percentage of anhydrous salt in next to last cryohydrate.
NaBr	-28°	-24°	8.1	41.33	41.61
NH ₄ I	-27	-27.5	6.4	55.49	57.6
NaI	-26.5	-15	5.8	59.45	59.39
KI	-22	-22	8.5	52.07	51.72
NaCl	-22	-22	10.5	23.60	
SrCl ₂ +6H ₂ O	-18	-17	22.9	27.57	27.5
NH ₄ ² SO ₄	-17.5	-17	10.2	41.70	42.2
NH ₄ Br	-17	-17	11.1	32.12	32.17
NH ₄ NO ₃	-17	-17.2	5.72	43.71	43.26
NaNO ₃	-16.5	-17.5	8.13	40.80	41.3
NH ₄ Cl	-16	-15	12.4	19.27	19.27
KBr	-13	-13	13.94	32.15	31.80
KCl	-10.5	-11.4	16.61	20.03	20.07
K ₂ CrO ₄	-10.2	-12	18.8	36.27	36.41
BaCl ₂ +2H ₂ O	-7.2	-8	37.8	23.2	24.0
Sr ₂ NO ₃	-6	-6	33.5	25.99	25.91
MgSO ₄ +7H ₂ O	-5.3	-5	23.8	21.86	
ZnSO ₄ +7H ₂ O	-5	-7	20.0	30.84	
KNO ₃	-3	-2.6	44.6	11.20	
Na ₂ CO ₃	-2.2	-2	92.75	5.97	
CuSO ₄ +5H ₂ O	-2	-2	43.7	16.89	
FeSO ₄ +7H ₂ O	-1.7	-2.2	41.41	16.92	17.35
K ₂ SO ₄	-1.5	-1.2	114.2	7.80	7.5
K ₂ Cr ₂ O ₇	-1	-1	292.0	5.30	
Ba ₂ NO ₃	-0.9	-0.8	259.0	5.30	
Na ₂ SO ₄ +10H ₂ O	-0.7	-0.7	165.6	4.55	
KClO ₃	-0.7	-0.5	222.0	2.93	2.88
Al ₂ NH ₄ 2SO ₄ +12H ₂ O	-0.4	-0.2	261.4	4.7	4.2
HgCl ₂	-0.2	-0.2	450.0	3.24	3.29

§ 89. *Remarks on Table*—The above Table contains the whole of the salts which I have as yet examined fully. The interesting group of the chlorides of the alkaline earths, including magnesium and the no less interesting group of the perchlorides of aluminium and iron, have presented difficulties with which I am still contending. The same is the case with the nitrate of calcium and the chloride of copper, Cu Cl_2 .

From the evidence before us I think, however, that I may venture to enunciate the general law, that if we define as similar salts either (1) those which consist of the same acid united with bases belonging to the same chemical group (ex. Na_2SO_4 , K_2SO_4), or (2) those which consist of the same base united with acids belonging to the same group (ex. KNO_3 , KClO_3), or (3) those whose bases belong to the same group, and whose acids belong to the same group—then, *of similar salts, the one which produces the greatest cold when used in a freezing-mixture unites as a cryohydrate with the fewest molecules of water*. And to the following law there seems to be only one pronounced exception: *The temperature at which the cryohydrate is formed is the same as the temperature of the corresponding freezing-mixture*. This latter law, however, has to be taken with reserve as far as those salts are concerned which, like AlCl_3 and MgCl_2 , decompose water, and also in regard to those bodies which, like CaCl_2 , unite with water under the liberation of much heat. These I shall consider in my next communication to the Society.

Cryohydrate of Ethylic Alcohol.

§ 90. Of very great interest is the behaviour which is shown by mixtures of ethylic alcohol and water when deprived of heat. This interest extends itself in a practical direction, in consequence of the use of alcoholic liquids in regions of extreme cold. We have here at once a new element for consideration. The two liquids are miscible in all proportions. This means that any possible hydrate of alcohol is soluble at ordinary temperatures both in water and in alcohol. I shall use the word alcohol to denote absolute alcohol, $\text{C}_2\text{H}_5\text{O}$, and the word "spirit" for a mixture of this with water.

§ 91. The fact so long known, that heat is liberated and volume finally lost when ethylic alcohol is mixed with water, has

silently pointed to the conclusion that there must be at least one definite hydrate of alcohol. It is sufficiently clear that if one were forced to the alternative of relying either upon the amount of heat liberated or upon the loss of volume, the former rather than the latter would be the most trustworthy.

§ 92. *Historical*.—A useful historical summary of much of what has been previously done in France in this direction of research is prefixed to a recent paper on the subject by M. Melsens, in the *Annales de Chimie et de Physique*, entitled “*Sur la refroidissement et la congélation des liquides alcooliques et des vins.*” According to M. Boussingault, frozen wines after thawing furnish an alcoholic liquid and are not therefore pure ice. According to M. Melsens, alcoholic liquids containing about 50 per cent. of alcohol by weight or by volume become at -30°C . viscid, syrupy, and sometimes opalescent. These represent commercial spirits such as rum, cognac, &c., and may be represented by the formula $\text{C}_2\text{H}_6\text{O} + 3\text{H}_2\text{O}$, corresponding to the maximum condensation. According, again, to M. Melsens, when wine which has become semisolid through being exposed to cold of a freezing-mixture is drained through wire gauze or introduced into a turbine, nearly colourless ice free from alcohol is left. From frozen wine containing from 10 to 12 per cent. of alcohol, from 16 to 25 per cent. of pure ice was got by means of a screw press. By the same means a frozen red or white Burgundy yielded 40 per cent. of ice.

§ 93. In the first of a series of able researches on the physical properties of mixtures of water with the alcohols, Messrs. Dupré and Page (Proc. Roy. Soc. March 11, 1869) examined, amongst others, the quantity of heat developed on mixing alcohol and water in various proportions, the specific heat of such mixtures, their capillarity, boiling-point, and their compressibility.

The following fragments of these experimenters' Tables include the critical values.

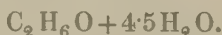
TABLE showing number of heat-units evolved from 5 grammes of mixtures resulting from mixing the percentages by weight of alcohol in column 1 with the complementary percentage of water. The asterisk shows the critical region.

per cent. alcohol.	Heat-units from 5 grms. of mixture.
10	26·68
20	43·95
30	47·98*
40	44·86
45	38·81

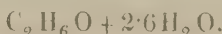
In the next Table Messrs. Dupré and Page's numbers are given, showing the specific heats of such mixtures. The column 1 shows the percentage of alcohol, column 2 the specific heat, column Δ the difference between the observed and calculated specific heats.

Alcohol per cent.	Specific heat.	Excess over calculated, Δ .
10	103·58	+ 7·53
20	104·36	12·27
30	102·60	14·47*
40	96·80	12·63
45	94·19	12·00
50	90·63	10·42

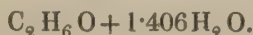
Messrs. Dupré and Page epitomize one branch of their research as follows:—"The whole of the physical characters of mixtures of alcohol and water come to a maximum deviation from their theoretical values somewhere between 30 and 45 per cent. of alcohol by weight. The 30 per cent. nearly corresponds to the formula $C_2H_6O + 6H_2O$ (29·87 per cent.); the 45 per cent. has approximately the formula $C_2H_6O + 3H_2O$ (46 per cent.)." The mean of these values is



§ 94. According to Rudberg (*Pogg. Ann.* vol. xiii. p. 496), the contraction is greatest when 55 volumes of alcohol are mixed with 45 volumes of water, or 43·6 weights of alcohol with 45 weights of water. This corresponds to the formula



§ 95. According to Bussy, alcohol not stronger than 33 Beaumé may be frozen by the evaporation of SO_2 . This strength is that of 78.29 per cent. of alcohol by weight, or



According to Marchand (*Journ. für Chemie*, vol. xxv. p. 253), when 1 part by weight of spirit is mixed with 1 part of snow, the depression of temperature depends upon the strength of the spirit, according to the following Table:—

per cent. by weight.	
90	−22°
70	−21
60	−19
50	−17.5
40	−16
30	−13
20	− 8

This is, I believe, the condition of the question as left by others.

§ 96. *My own experiments.*—The alcohol I used was shaken with dry carbonate of potassium and distilled from quicklime. With this I made decimal mixtures ranging from 95 alcohol and 5 of water to 95 water and 5 of alcohol. These were submitted in turn to the action of a cryogen, in order first of all to see at what temperature the solidification of each mixture *begins*. For if, as has been supposed, and quite recently by Melsens again proved, a very weak (10 per cent.) spirit gives up only ice, and since alcohol is notoriously not to be solidified by our most powerful cryogens, it must follow that during the continuous solidification of a weak spirit the temperature must fall continually. Temperatures down to -19° were observed on the mercurial thermometer. For lower temperatures, demanding the employment of solid carbonic acid and ether, use was made of an alcohol thermometer, which was collated with the mercurial one at -22° . The Table gives the temperature at which the solution began to yield solid matter. What this solid matter consists of I have afterwards to consider. Columns Δ_1 and Δ_2 are the values of the first and second differences respectively.

TABLE XI.—Temperatures at which Solidification begins in Spirits of various strengths.

Water per cent., by weight.	Alcohol per cent., by weight.	Temperature C. at which solidification begins.	Δ_1 .	Δ_2 .
95	5	— 2°	2.3	+0.6
90	10	— 4.3	2.9	+0.6
85	15	— 7.2	3.5	+0.5
80	20	—10.7	4.0	+0.7
75	25	—14.7	4.7	—0.8
70	30	—19.4	3.9	—0.2
65	35	—23.3	3.7	+0.3
60	40	—27	4.0	+2.0
55	45	—31	6.0	—1.0
50	50	—37	5.0	—2.0
45	55	—42	3.0	+5.0
40	60	—45	8.0	?
35	65	—53	?	
30	70	—65 (not).		

From this Table it is seen that the temperature of initial solidification sinks so regularly that the column of second differences shows for a long time the value 0.6. Only at lower temperatures, which of course cannot pretend to the same degree of accuracy, are serious variations visible. There is a rapid fall at the ratio 35 water to 65 alcohol; and at the ratio 30 water to 70 alcohol, I failed to effect solidification at -65° C.

§ 97. So free from discontinuity are these numbers, that one might be readily misled into the belief that the solid matter separated is in all cases ice. This, however, is not the case. Down to the ratio 65 water and 35 alcohol, the ice spicula freely moving in the mother-liquid are easily recognized. If they are remelted they invariably reform at the same temperature. At ratios of 60 water to 40 alcohol and stronger, the aspect of the solid formed is quite different. The liquid may then acquire the consistency of Canada balsam, and yet, if kept still, it may remain perfectly transparent. On rubbing with the thermometer-bulb or with a glass rod minute crystals are formed, the liquid becomes more mobile, resembling old honey. It offers a notable case of a condition of supersaturation producing a temporary colloid condition.

§ 98. Finding that this phenomenon was first noticeable at about the solution of the ratio 60 water to 40 alcohol, and reflect-

ing that this is nearly the ratio of one molecule of alcohol to four of water, I made a spirit of exactly this molecular ratio, namely 39·07 alcohol and 60·93 of water by weight. On submitting this to the action of a cryogen, I found the remarkable result that nothing separated till the temperature -34° was reached, although both weaker and stronger solutions begin to solidify at higher temperatures. The solid formed in this case is perfectly white and opaque, and the temperature remains constant till the whole has become perfectly dry. This pearly aspect and the constancy of temperature throughout the solidification betray the cryohydrate. Both weaker and stronger spirits sink in temperature as they solidify—the former until by the elimination of ice it presents a mother-liquor of the 4-hydrate composition, the latter by the elimination of liquid alcohol as the solid 4-hydrate is formed.

§ 99. When, therefore, a dilute alcohol (say 95 water to 5 alcohol) is cooled, ice separates out, the spirit becomes stronger and stronger, and the temperature lower and lower. When the ratio $C_2H_6O + 4H_2O$ is reached the temperature $-34^{\circ} C.$ is reached, and the remainder of the solution is a cryohydrate of alcohol whose melting- and freezing-point is -34° , and whose composition is $C_2H_6O + 4H_2O$.

On the other hand, if a spirit a little stronger than $C_2H_6O + 4H_2O$ is subjected to cold, nothing separates till about $-27^{\circ} C.$ At this temperature the cryohydrate $C_2H_6O + 4H_2O$ begins to separate out, and as it relinquishes the alcohol the solidifying-point of the mother-liquor falls. Observe, the cryohydrate separates from alcohol at a temperature above its own melting-point when alone. It follows from this that solidification may commence at the same temperature in two spirits of different strengths, provided they are both close about the 4-molecule hydrate in composition. But while in the weaker the solid will be ice, in the stronger it will be the cryohydrate. The apparent anomaly arises from the circumstance that the cryohydrate is soluble both in water and alcohol, and that ice is soluble in the liquid cryohydrate. We are here reminded of the phenomenon of the maximum density of water, which I have already endeavoured to connect with the formation of a cryohydrate of water (in § 36).

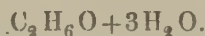
§ 100. For some reasons this melted cryohydrate of alcohol, or spirit of wine containing 60·93 water and 39·07 of alcohol, should be the standard or proof spirit in all alcoholometry.

English proof spirit contains 50·5 per cent. by weight of alcohol. It accordingly should begin to solidify at -38° (about the freezing-point of mercury). At lower temperatures it becomes a pasty mass, but never perfectly brittle, on account of the unfreezable alcohol in excess above that of the cryohydrate. Spirits of 39 per cent. and under become perfectly solid before the temperature reaches -36° . The very fact that weaker spirits wholly solidify while stronger never do so is, I conceive, a complete proof of the existence of a cryohydrate. For if under all circumstances water alone solidified, alcohol would be left even from the weakest spirits, and total solidity could never be reached.

§ 101. The above considerations, of course, only apply to the chemically pure substances alcohol and water; how far the sugar, caramel, fusel, essences &c. of commercial spirits, and the innumerable substances in wines and beers may affect the solidification is a matter for future research. It is quite possible, for instance, that in some rums the 10 per cent. alcohol above that required for the cryohydrate might find sufficient foreign matter present to form therewith a solid, and so allow the whole to solidify.

§ 102. I believe that the detection of this 4-molecule hydrate of alcohol reconciles the apparently contradictory results of former experimenters. Thus, looking on wine as a 10-per-cent. spirit of wine, M. Melsens obtained by a freezing-mixture 40 per cent. of ice. I judge from Table XI. that the temperature reached was -8° , if we make no allowance for loss of ice during manipulation.

§ 103. The evidence adduced by Messrs. Dupré, Page, and others points to the existence of at least one hydrate of alcohol; but I am not prepared to say that such hydrate is necessarily identical with the 4-molecule cryohydrate which we have been considering. It must be remembered in this connexion that the cryohydrates of solid salts contain more water than any other known hydrate; and the existence of the 4-molecule cryohydrate rather, I conceive, tends to show that the ordinary hydrate of alcohol contains less water, and is, as some of Dupré and others' experiments may be interpreted as showing, the 3-hydrate



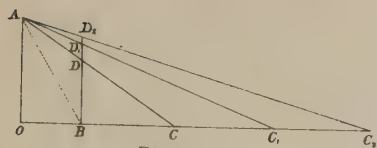


Fig. 1.

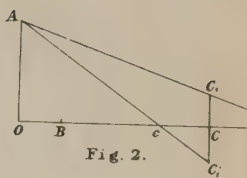


Fig. 2.

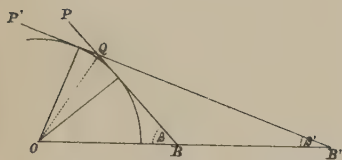


Fig. 4.

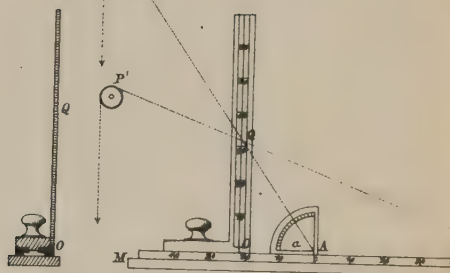


Fig. 5a.

Fig. 5.

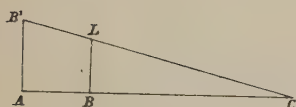


Fig. 7.

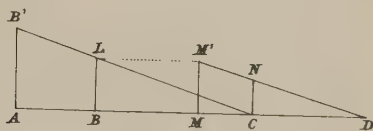


Fig. 8.

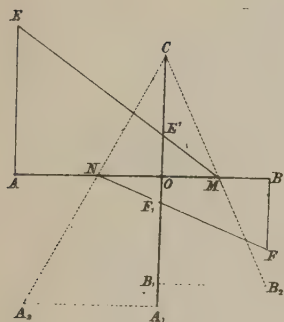


Fig. 11.

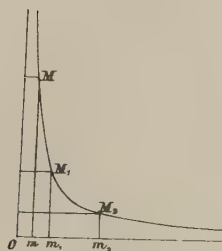


Fig. 12.

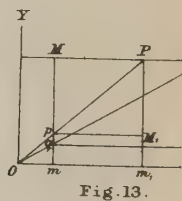


Fig. 13.



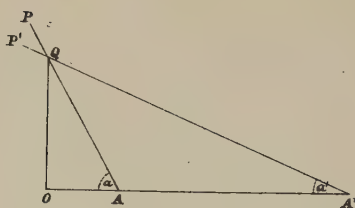


Fig. 3.

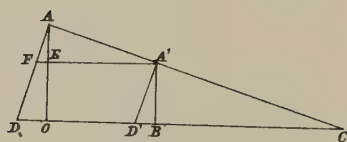


Fig. 6.

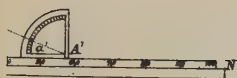


Fig. 9.

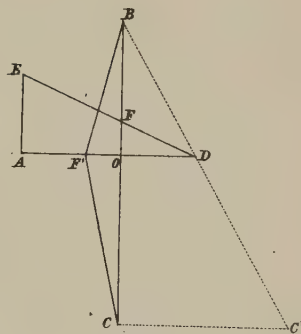


Fig. 10.

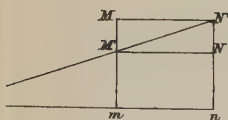


Fig. 14.

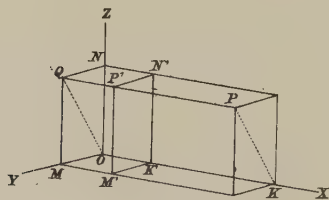


Fig. 15.

Cryohydrate of Ether.

§ 104. *Cryohydrate of Ether* (?).—It is well known that when water and ethylic ether are shaken together mutual but only partial mixture ensues, the water taking up about one ninth of its volume of ether, and the ether about one thirty-sixth of its volume of water. Such an aqueous solution of ether when subjected to cold, solidifies at -2° C., without any separation of ether, into a dry solid consisting of ether and water. The compound exhibits an interesting feature, inasmuch as it exemplifies the effect of cooling on the luminosity of flame. The cryohydrate of ether may be solidified in a long test-tube, and thence removed, presenting the appearance of a candle. One end of this is cut off flat, and the whole placed upright on a plate. A light being applied at the top, the whole melts away as the ether burns. The flame is quite non-luminous. The ether is only free to burn as it is in the act of melting ice, and is so cooled. So it is well known that marsh-gas becomes luminous if heated before combustion. Thus ether (which is empirically olefiant gas plus water) and alcohol (which is empirically ether plus water) have flames of luminosity the less according as their ratio of potential water is greater. The cryohydrate of ether is in fact physically, as far as its luminosity is concerned, an alcohol.

Throughout this second part of this research I have been much indebted to my friend Mr. R. Cowper for his very zealous and skilful assistance.

XIV. *On Graphical Methods of solving certain simple Electrical Problems.* By Prof. G. CAREY FOSTER, F.R.S.*

[With a Plate.]

It is probably very seldom that the geometrical representation of the mathematical relations between physical quantities is as convenient, for purposes of investigation, as the corresponding analytical expression; but for purposes of exposition, as distinguished from those of investigation, geometrical constructions often possess considerable value. In particular, whenever they can be put into a simple form, their physical significance

* Read November 7, 1874.

is more easily understood, than that of an algebraical formula, by those who are but little accustomed to mathematical modes of expression; and they generally exhibit with greater clearness the effect of a variation of any one of the related magnitudes. I have therefore thought that it might be worth while, for the sake of trying to draw increased attention to the utility of geometrical methods in elementary physical teaching, to point out in detail their application to a few important electrical problems, such as some of the simplest cases which come under Ohm's law of the relations between electromotive force, strength of current, and resistance.

If the equation which expresses Ohm's law be written in the three following ways—

$$\frac{E}{C} = R, \quad \frac{E}{R} = C, \quad CR = E,$$

where E stands for *electromotive force*, C for *strength of current*, and R for *resistance*, we have at once suggested three different modes of geometrical construction by means of rectangular co-ordinates, the coordinates representing in the three cases respectively (1) electromotive force and strength of current, (2) electromotive force and resistance, and (3) strength of current and resistance.

I. *Ordinates represent Electromotive Forces, and Abscissæ represent Strengths of Current.*

This system, according to which *resistance* comes to be represented by the *slope* of a straight line (that is, by the tangent of the angle which the line makes with the axis of abscissæ), was lately employed by M. Crova* for the discussion of experiments relating to the degree of constancy possessed by so-called “constant” galvanic batteries; and its application to several other problems, including some of those treated by other methods in this paper, has been still more recently† pointed out by the same author. It is therefore not needful to discuss it further in this place.

* *Comptes Rendus*, 6th April 1874, vol. lxxviii. p. 965.

† *Journal de Physique* (Sept. 1874), vol. iii. p. 278.

II. Ordinates represent Electromotive Forces, and Abscissæ represent Resistances.

This system was used long ago by Ohm*, and has been frequently employed since his time, though perhaps chiefly by practical electricians†. The following examples may serve to illustrate its application to questions connected with galvanic circuits in which there is a constant electromotive force.

Let $O A$ (Plate III. fig. 1) represent the electromotive force of a battery, $O B$ the resistance of the battery, and $B C$ the resistance of the remainder of the circuit, this being made up of simple metallic conductors in which no additional electromotive force acts, then the slope of the straight line $A C$, or the *tangent* of the angle $A C O$, represents the strength of the current. It is obvious, by a glance at the figure, that the strongest current that the given battery could produce would be obtained by making the external resistance $B C$ equal to nothing, and that it would be represented by the slope of the line $A B$, or by $\tan \angle A B O$. Also it is evident that, if the external resistance is increased by equal amounts $C C_1, C C_2, \dots$ each equal to $B C$, the strength of the current, as denoted by the slope of the line drawn from A to the points $C, C_1, C_2, \dots$, diminishes by smaller and smaller amounts for each equal increment of resistance, and that it would not vanish for any finite value of the resistance.

If any electromotive force acts in the part of the circuit external to the battery, its effect on the strength of the current can be represented by drawing through C a line $C C'$ parallel to $O A$, and of length proportional to the external electromotive force, *upwards* if this electromotive force is *inverse*, *downwards* if it is *direct*,—and drawing the straight line $A C'$ (fig. 2). If c be the point where this line cuts $O C$, $\tan \angle A c O$ measures the strength of the current. Of course the effect of any electromotive force outside the battery could also be represented by a diagram such as fig. 1, if the line $O A$ were there taken to repre-

* *Die galvanische Kette mathematisch bearbeitet*, 1827.

† See, for example, R. S. Culley, 'Handbook of Practical Telegraphy,' 1874, pp. 352-355; Latimer Clark, 'Elementary Treatise on Electrical Measurements,' 1868; G. K. Winter, "On Earth-Currents," *Journal of the Society of Telegraph-Engineers*, vol. ii. pp. 89-101; &c.

sent, not the electromotive force of the battery, but the total resultant electromotive force of the whole circuit.

If a line be drawn from B (fig. 1) parallel to O A, the length $BD, BD_1, BD_2 \dots$ intercepted by the straight line through A, whose slope gives the strength of the current, represents the difference of potential between the terminals of the battery, or, in other words, the electromotive force which is effective in maintaining a current in the external conductor. The figure shows that this varies between a maximum ($=OA$, the total electromotive force of the battery) when the external resistance is infinite (contact broken) and a minimum ($=0$) when the external resistance is nothing. If two values, BD and BD_1 , of the externally effective electromotive force are known, which correspond respectively to two known values BC and BC_1 of the external resistance, it is evident that the electromotive force and internal resistance of the battery will be given by drawing the straight lines CD and C_1D_1 , producing them till they meet in A, and letting fall from A a perpendicular AO on CB produced: AO and OB then represent respectively the values required. Experimentally, the values to be given to BD and BD_1 could be found by direct measurement with an electrometer; or they could be got from the relation $e' = cr'$, where e' is the externally effective electromotive force and c the current as measured by a galvanometer in a circuit of external resistance $=r'$.

From the above relations it is easy to deduce a construction, which may sometimes be of practical use, *for finding the permanent resistance and electromotive force of a constant battery from two deflections of a galvanometer without using trigonometrical tables*. This construction requires to be slightly modified according to whether the instrument used is a tangent-galvanometer or a sine-galvanometer. It is as follows:—

1. *For a tangent-galvanometer*.—The battery is connected in simple circuit with a tangent-galvanometer, and the deflection α of the galvanometer is observed; then a known resistance r' is added to the circuit and the deflection is observed again. Let the second deflection be denoted by α' . The following construction then gives the electromotive force of the battery ($=e$) and the permanent resistance of the circuit ($=r$).

From any point A in the straight line O A (fig. 3) draw A P,

making the angle $\angle OAP = \alpha$; produce OA to A' , making AA' proportional to the added resistance r' , and from A' draw $A'P'$, making the angle $\angle OA'P' = \alpha'$ and on the same side of OA as AP . Since α' is less than α , the straight lines AP and $A'P'$ will intersect. From the point of intersection Q draw QO perpendicular to OA . Then OA represents the permanent resistance of the circuit, and QO represents the electromotive force, in terms of that electromotive force taken as unity which, if it acted in a circuit of unit resistance, would generate a current capable of causing a deflection of 45° on the particular galvanometer employed.

2. *For a sine-galvanometer.*—Let β be the deflection observed when there is no extra resistance, and β' the deflection when an additional resistance r' has been inserted in the circuit. Make BB' (fig. 4) proportional to r' , make the angles $\angle OBP$ and $\angle OB'P'$, on the same side of BB' , equal respectively to β and β' , and let BP and $B'P'$ intersect at the point Q . Draw QO to bisect the external angle $\angle BQP'$, and cutting $B'B$ produced in O ; then OB represents the permanent resistance of the circuit, while the radius of a circle drawn with the point O as centre so as to touch the straight lines BP and $B'P'$ measures the electromotive force, the unit of measurement for the latter being the electromotive force which, in a circuit of unit resistance, would give a current strong enough to deflect the galvanometer used through 90° .

If the constructions indicated above are carried out for several different values of the external resistance, it is clear that, with a strictly constant battery, lines drawn according to the same rule as AP and $A'P'$, in the case of a tangent-galvanometer, will all pass through the same point, and that, in the case of a sine-galvanometer, all lines drawn in the same way as BP and $B'P'$ will be tangents to the same circle.

These constructions are so simple and can be so quickly

* It may be worth while to point out that any galvanometer may be used as a sine-galvanometer, even though it is not provided with a graduation to show the angle through which it has been turned. It is only needful, after setting the instrument so that the zero of the scale is exactly below the needle while the current is passing, to interrupt the current; the needle then swings away from the zero-mark, returning to the magnetic meridian; and the angle now indicated by it is the angle through which the galvanometer has been turned from the meridian.

made with sufficient accuracy, that by means of them the effect of altering the resistance of a circuit or the number or arrangement of the cells of a battery can be exhibited to a class by the help of actual measurements made during a lecture; but in order to make the process still more rapid, I have had an apparatus made, which may be called "A Galvanometric Slide-Rule," whereby, when two deflections of a galvanometer have been observed corresponding to a known difference of resistance, the permanent resistance and electromotive force of a battery can be ascertained in the course of a few seconds. The general arrangement of this apparatus is shown in fig. 5, which is drawn to a scale of about $\frac{1}{2}$. MN is a wooden base about 155 centims. long by 15.2 centims. wide, and 4.7 thick, with a groove in the upper surface, of the shape shown in fig. 5a, running from end to end. On the vertical side shown in the figure there is a scale 150 centims. long, divided into millimetres and numbered towards right and left from zero at a point A 50 centims. from M and 100 centims. from N. Exactly above the zero mark of the scale is a small brass stud, the axis of which passes through the centre of a small graduated quadrant of 12 centims. radius. Another, similar quadrant, A', with a brass stud at the centre is attached to a small board which slides on the upper side of MN and can be clamped by a screw in any position between A and N. There is also a vertical scale 65 centims. long, divided into millimetres and numbered from the bottom upwards, which is fastened to a sliding piece C, whereby it can be clamped in any position between M and A. The faces of the vertical scale and of the quadrants A and A' are flush with the face of the horizontal scale MN. Two thin silk cords, stretched by small weights, are passed over pulleys at P and P', and attached one to each of the pins at the centres of the quadrants A and A'. The pulleys are so placed that the cords are very nearly in the same vertical plane as the scales MN and CQ. The apparatus is used as follows:—The pulley P is raised or lowered until the cord fixed at A shows, upon the corresponding quadrant, the deflection obtained on the tangent-galvanometer when no extra resistance is added to the circuit; the sliding piece carrying the quadrant A' is then moved towards right or left so that the number of centimetres in the distance AA' may be the same as the number of units of resistance (or, if more convenient, so

that it may be a simple multiple or submultiple of this number) added to the circuit in order to get a second reading of the galvanometer; then the pulley P' is adjusted so that the cord passing over it may indicate upon the quadrant B the galvanometer-deflection obtained after introducing the resistance corresponding to $A A'$; and lastly the vertical scale is moved so that a vertical line drawn through the centre of the division-marks and continued downwards to meet the horizontal scale at O may be exactly behind the point Q , where the cords $A P$ and $A' P'$ cross each other. We have then only to read off the horizontal and vertical distances, $A O$ and $O Q$, to get the permanent resistance and electromotive force of the circuit*. To adapt the apparatus to use with a *sine-galvanometer*, it would be only necessary to replace the vertical scale $O Q$ by a quadrant marked with concentric circular arcs, each differing from the next by 1 millim. in radius.

The following additional examples may be given of the same mode of treatment in connexion with allied problems:—

Development of Heat in a Galvanic Circuit.—Draw OC (fig. 6) horizontally to represent the resistance of the circuit, and OA vertically to represent the electromotive force; from A draw AC and also AD at right angles to AC ; then OD represents the heat produced in the circuit per unit of time. It is of course to be understood that OA denotes not necessarily the electromotive force of the battery, but the resultant electromotive force of the whole circuit—that is, the algebraic sum of all the electromotive forces which act anywhere in it. If OB denote the resistance of the battery and BC the remaining resistance of the circuit, and if BA' be drawn vertically, $A'E F$ horizontally, and $A'D'$ at right angles to AC , $E F$ will denote the heat generated in the battery, and $B D'$ the heat generated in the external part of the circuit.

Strength of Currents in the different branches of a divided Circuit.—In considering this problem it is needful first of all to have a mode of representing geometrically the combined resistance of two or more conductors connected in “multiple arc.” Let AB and BC in the same straight line (fig. 7) represent the resis-

* The quadrant A is made so that it can be turned aside to allow of the vertical scale being brought close up to the zero-point of the horizontal scale when low battery-resistances have to be measured.

tances of two conductors taken separately. Draw AB' equal to AB and at right angles to it; join $B'C$, and through B draw a line parallel to AB' and cutting $B'C$ in L ; then BL represents the combined resistance of the two conductors. The same process is applicable to any number of conductors. Thus, let AB , BC , and CD (fig. 8) represent the separate resistances of three conductors connected in multiple arc. Making the construction indicated above, BL represents the resistance equivalent to AB and BC in multiple arc. Draw LM' parallel to $ABCD$, make $CM = BL$, draw MM' at right angles to BC , join $M'D$, and draw CN perpendicular to CD . CN then represents the joint resistance of the three conductors.

Now consider a conducting-system such as that indicated in fig. 9, where two points, P and Q , are connected through three conductors whose resistances are respectively r , r_1 , and r_2 ; and let a battery of electromotive force e make part of the first conductor. The strength of the currents and the distribution of potential in the various parts of the system can be represented as follows:—Take OA (fig. 10) to represent r , from O draw OB and OC in opposite directions perpendicular to OA , make CC' equal to OC and perpendicular to it, draw BC' cutting AO produced in D ; then OD represents the joint resistance of r_1 and r_2 . Draw AE perpendicular to AO to represent the electromotive force e , and join ED . Then $\tan \angle ADE$ represents the strength of the current in the battery and the sum of the currents in the two parallel branches. These may be obtained separately thus: let the point of intersection of ED and OB be denoted by F ; then OF represents the difference of potential between the points P and Q or the electromotive force which is effective in the two conductors of resistance r_1 and r_2 . In OA make $OF' = OF$ and draw $F'B$ and $F'C$; we have then, for the strength of the currents in the conductors whose resistances are represented by OB and OC , $\tan \angle OBF'$ and $\tan \angle OCF'$ respectively.

Next let *two* of the conductors connected together at P and Q contain galvanic batteries, and, as before, let the resistance of the branch containing one battery be r , while that of the branch containing the other is r_1 , and let the electromotive forces be e and e_1 respectively. If the batteries are so connected that both tend to make the potential at P differ from that at Q in the same

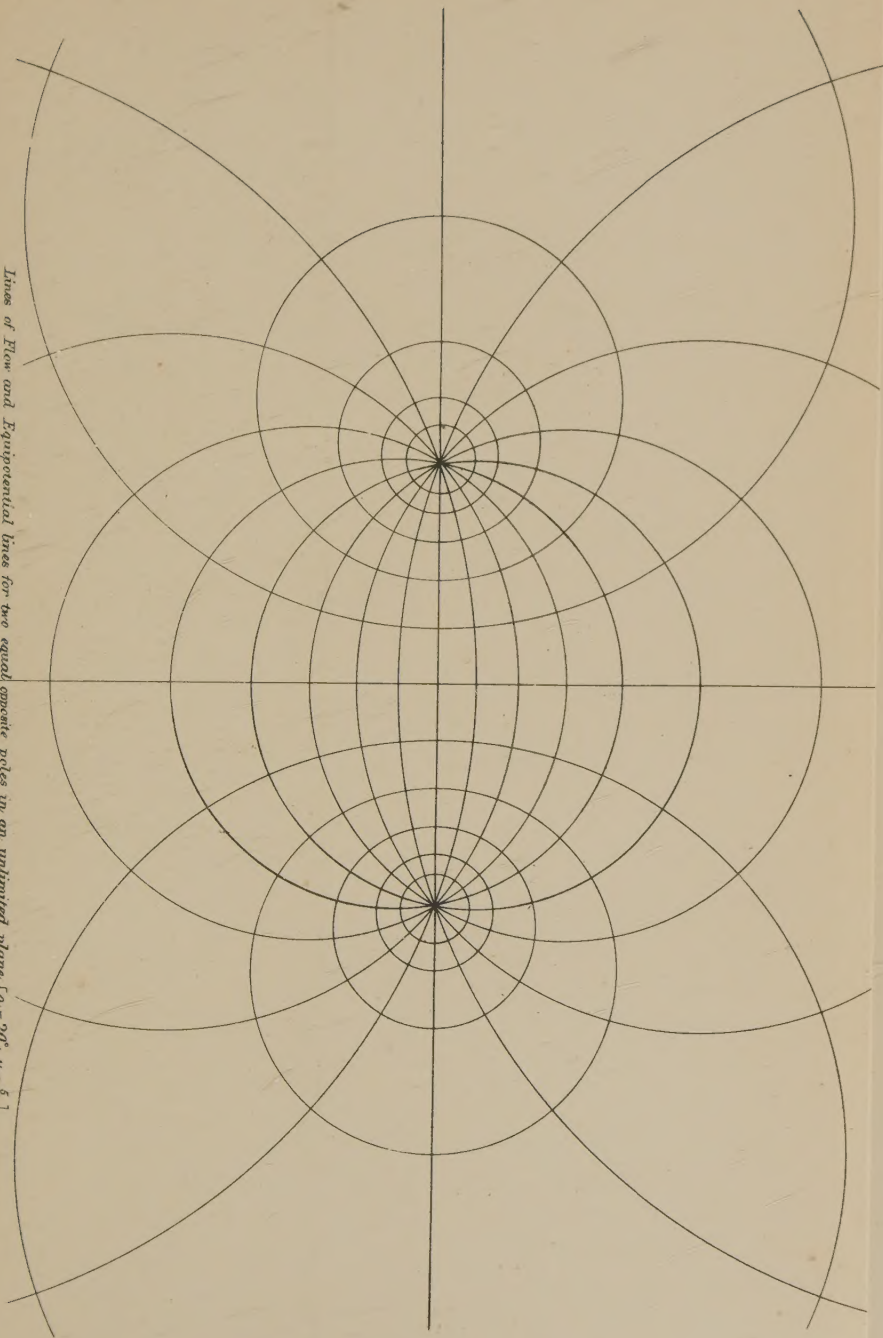
sense, we have an arrangement of which a special case is presented by Poggendorff's "compensation method" for the comparison of electromotive forces. To obtain a geometrical expression for the strengths of the currents in the various parts of the circuit in the general case (that is, without assuming that there is "compensation" in any branch), we may proceed in the following manner:—Take OA and OB in the same straight line (fig. 11) to represent the resistances r and r_1 of the two branches including the batteries, and OC at right angles to AB to represent the resistance r_2 of the third branch. In CO produced make $OA_1 = OA$, and $OB_1 = OB$, also draw A_1A_2 equal and parallel to OA and B_1B_2 equal and parallel to OB , and join A_2C and B_2C . Let A_2C cut OA in N , and let B_2C cut OB in M . From A draw AE at right angles to AO to represent the electromotive force e , and draw EM cutting OC in E' ; similarly, from B draw BF^* to represent the electromotive force e_1 , and draw FN cutting CO (produced) in F' . Then $F'E' = F'O + OE'$ represents the electromotive force which is effective in the conductor of resistance r_2 represented by OC , and $AE - F'E'$ and $FB - F'E'$ represent the electromotive forces which are effective in the branches of resistance r and r_1 respectively.

III. *Ordinates represent Strength of Current, and Abscissæ represent Resistances.*

With this system of coordinates, electromotive force is expressed by the area of a rectangle. Thus, if a given battery produces a current whose strength is represented by the ordinate Mm of the point M (fig. 12), in a circuit the resistance of which is represented by the abscissa Om of the same point, its electromotive force must be proportional to the area of the rectangle OM ; and if the battery is "constant," the currents, represented by the ordinates M_1m_1 , M_2m_2 , and corresponding to the resistances denoted by the abscissæ Om_1 , Om_2 , will be such that the areas of the rectangles OM , OM_1 , and OM_2 are all equal; and hence the characteristic property of the battery will be expressed by the curve which is the locus of the points M , M_1 , &c.—that is to say, by a rectangular hyperbola whose asym-

* BF must be drawn in the *opposite* direction to AE if, as supposed above, the batteries are so connected that the difference of potential between the points P and Q due to each battery separately is of the *same* sign.

Lines of Flow and Equipotential lines for the equal opposite poles in an unbounded plane [$\alpha = 30^\circ$, $w = \frac{1}{2}$]



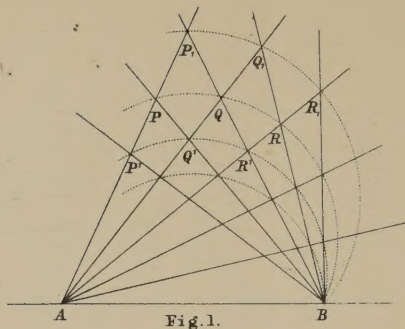


Fig. 1.

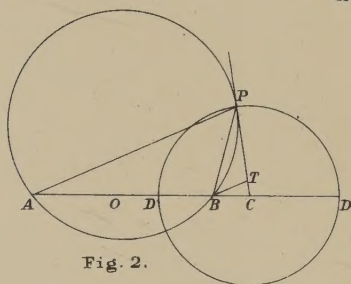


Fig. 2.

- $AO - OB = a$
- $OC = d$
- $BC = h$
- $OD = l$
- $OD' = l'$
- $CP = \ell$
- $AP = r$
- $BP = r'$

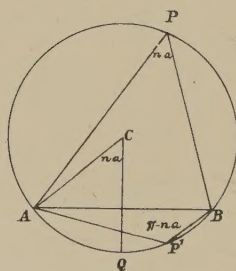


Fig. 3.

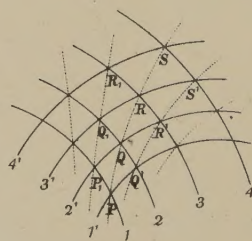
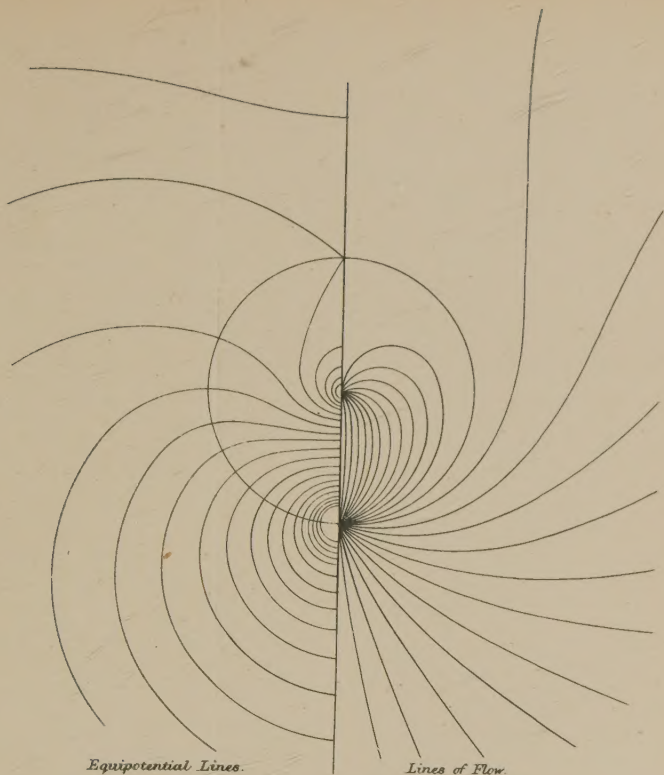


Fig. 4



Two opposite poles, one twice as strong as the other.

Fig: 6.

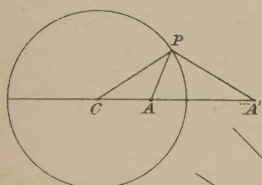


Fig: 5.

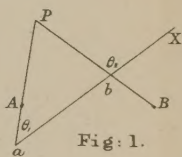
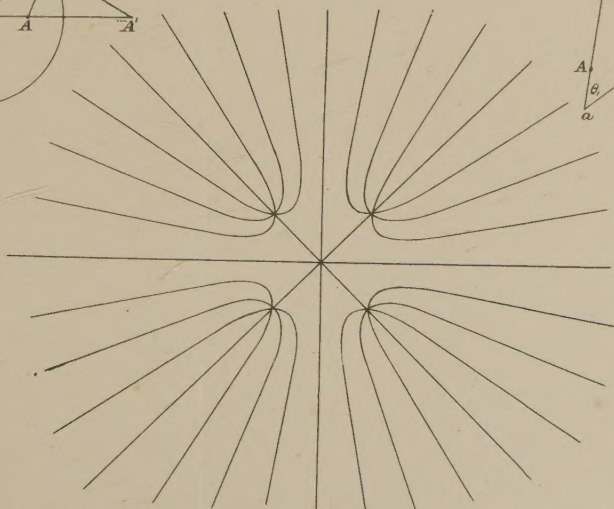
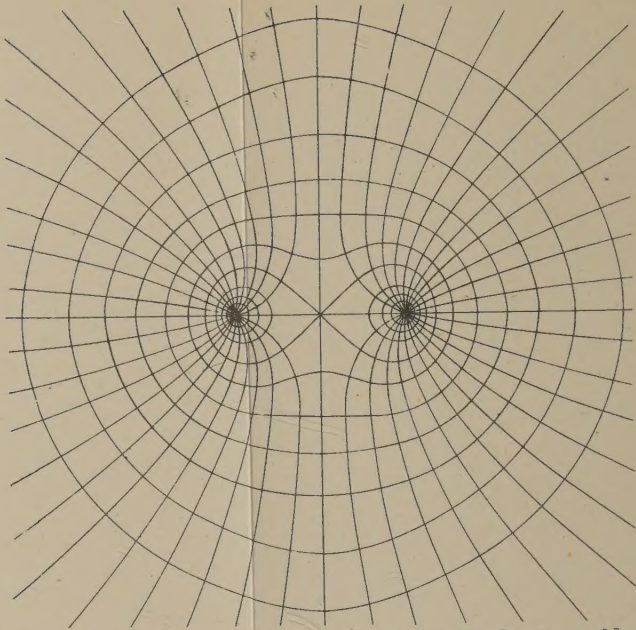


Fig: 1.

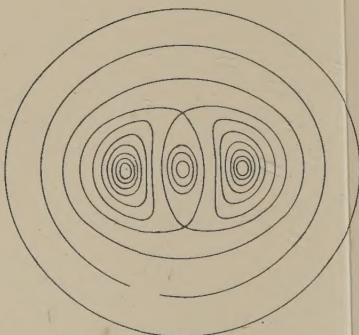


Four Equal Similar Poles.

Fig: 7.



Lines of Flow and Equipotential Lines for two equal Similar Poles. [$a=15^\circ$; $\mu=\frac{3}{2}$]
Fig: 3.



Loci of Equal Flow for two equal Similar Poles.
Fig: 4.

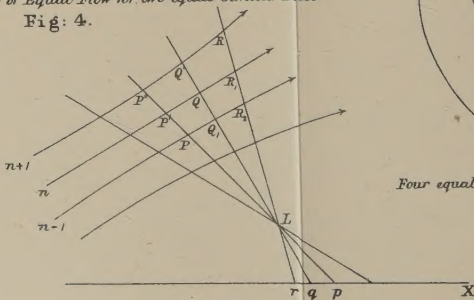
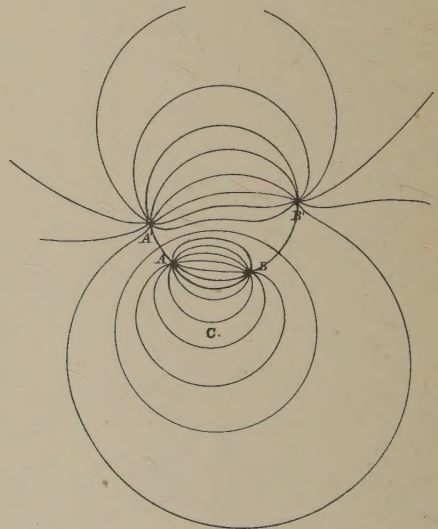


Fig: 2.



Four equal Poles: A and A' positive; B and B' negative.
Fig: 9.